

IN THE UNITED STATES DISTRICT COURT  
FOR THE DISTRICT OF DELAWARE

CALLAWAY GOLF COMPANY,

Plaintiff,

v.

ACUSHNET COMPANY,

Defendant.

C. A. No. 06-91 (SLR)

**PUBLIC VERSION**

**DECLARATION OF THOMAS L. HALKOWSKI IN SUPPORT OF CALLAWAY  
GOLF COMPANY'S *RESPONSE* TO ACUSHNET'S OPENING BRIEF IN SUPPORT  
OF ITS PROPOSED CLAIM CONSTRUCTIONS**

I, Thomas L. Halkowski, declare as follows:

1. I am a principal of Fish & Richardson P.C., counsel of record in this action for Callaway Golf Company. I am a member of the Bar of the State of Delaware and am admitted to this Court. I have personal knowledge of the matters stated in this declaration and would testify to them under oath if called upon to do so.

2. Attached as **Exhibit 1** is a true and correct copy of the Declaration of Jeffrey L. Dalton dated January 5, 2006 and filed in the Request for Reexamination as it relates to U.S. Patent 6,506,130.

3. Attached as **Exhibit 2** is a true and correct copy of the Declaration of Jeffrey L. Dalton dated January 5, 2006 and filed in the Request for Reexamination as it relates to U.S. Patent 6,210,293.

4. Attached as **Exhibit 3** is a true and correct copy of the Declaration of Jeffrey L. Dalton dated January 5, 2006 and filed in the Request for Reexamination as it relates to U.S. Patent 6,595,873.

5. Attached as **Exhibit 4** is a true and correct copy of the Declaration of Jeffrey L. Dalton dated January 5, 2006 and filed in the Request for Reexamination as it results to U.S. Patent 6,503,156.

6. Attached as **Exhibit 5** is a true and correct copy of
7. Attached as **Exhibit 6** is a true and correct copy of **REDACTED**
- 8 Attached as **Exhibit 7** is a true and correct copy of
9. Attached as **Exhibit 8** is a true and correct copy of
10. Attached as **Exhibit 9** is a true and correct copy of the United States Patent No. 5,492,972. (CW00506650-655.)
11. Attached as **Exhibit 10** is a true and correct copy of the United States Patent No. 6,634,964. (AC0099071-083.)
12. Attached as **Exhibit 11** is a true and correct copy of the United States Patent No. 6,818,705. (AC0018866-885.)
13. Attached as **Exhibit 12** is a true and correct copy of the United States Patent No. 6,849,006. (AC0097292-304.)
14. Attached as **Exhibit 13** is a true and correct copy of the United States Patent No. 6,960,630. (AC0097339-351.)
15. Attached as **Exhibit 14** is a true and correct copy of the United States Patent No. 6,100,340.

I declare under penalty of perjury that the foregoing is true and correct.

Executed this 27th day of August, 2007 at Wilmington, Delaware.

/s/ Thomas L. Halkowski  
Thomas L. Halkowski

**CERTIFICATE OF SERVICE**

I hereby certify that on September 4, 2007, the attached document was electronically filed with the Clerk of Court using CM/ECF which will send electronic notification to the registered attorney(s) of record that the document has been filed and is available for viewing and downloading.

I hereby certify that on September 4, 2007, I have Electronically Mailed the document to the following person(s):

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David E. Moore  
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Attorneys for Defendant  
ACUSHNET COMPANY

/s/ Thomas L. Halkowski  
Thomas L. Halkowski

# Exhibit 1

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re U.S. Patent No.: 6,506,130

Inventor: Michael J. SULLIVAN

Issued: January 14, 2003

Appl. 09/832,154

Filed: December 21, 1999

Titled: **MULTI LAYER GOLF BALL**

**REQUEST FOR REEXAMINATION  
UNDER 35 U.S.C. §§ 301-307, 314 AND  
37 C.F.R. §§1.913-1.914**

**DECLARATION OF JEFFREY L. DALTON UNDER 37 C.F.R. § 1.132**

I, Jeffrey L. Dalton, Vice President of Product Development at the Acushnet Company Fairhaven, Massachusetts, hereby declare as follows:

1. I am employed Acushnet Company, located at 333 Bridge Street, Fairhaven, Massachusetts 02719.
2. My current job title is Vice President of Product Development.
3. I am familiar with the polyurethane material that is described in Example 1 of United States Patent No. 5,334,673 to Shenshen Wu ("Wu"). This composition is reproduced below:

**TABLE I**

	<b>Grams</b>
<b>MDI prepolymer*</b>	<b>100.00</b>
<b>Polamine 250**</b>	<b>48.87</b>
<b>White Dispersion</b>	<b>5.21</b>

\*MDI prepolymer is 4,4'-diphenylmethanediisocyanate with a polyol of polytetramethylene ether glycol.

\*\*Polamine 250 is polytetramethyleneoxide-di-p-aminobenzoate having a molecular weight of about 476 g/m.

Rule 132 Declaration of Jeffery L. Dalton  
Submitted in Support of Acushnet's request for *Inter Partes* Reexamination of U.S. Patent No. 66,506,130

Page 2

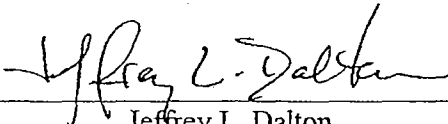
4. The polyurethane material described in Example 1 of the Wu was used as the outer cover layer material on the Titleist® Professional® golf ball from 1993 until 2002, when Acushnet stopped manufacturing the Professional™ golf ball.

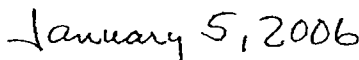
5. I am familiar with the mechanical properties of the polyurethane materials described in the Wu patent.

6. The polyurethane material described in example 1 of the Wu patent had a Shore D hardness of about 58 Shore D when tested according to ASTM standards on the cover of a ball.

7. The polyurethane material described in example 1 of the Wu patent had a flexural modulus of about 23,000 psi when tested according to ASTM standards.

8. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

  
\_\_\_\_\_  
Jeffrey L. Dalton

  
\_\_\_\_\_  
Date

# Exhibit 2

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re U.S. Patent No.: 6,210,293

Inventor: Michael J. SULLIVAN

Issued: April 3, 2001

Appl. 09/470,196

Filed: December 21, 1999

Titled: **MULTI-LAYER GOLF BALL**

**REQUEST FOR REEXAMINATION  
UNDER 35 U.S.C. §§ 301-307, 314 AND  
37 C.F.R. §§1.913-1.914**

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	Grams
MDI prepolymer*	100.00
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\*MDI prepolymer is 4,4'-diphenylmethanediisocyanate with a polyol of polytetramethylene ether glycol.

\*\*Polamine 250 is polytetramethyleneoxide-di-p-aminobenzoate having a molecular weight of about 476 g/m.

Rule 132 Declaration of Jeffery L. Dalton  
Submitted in Support of Acushnet's request for *Inter Partes* Reexamination of U.S. Patent No. 6,210,293

Page 2

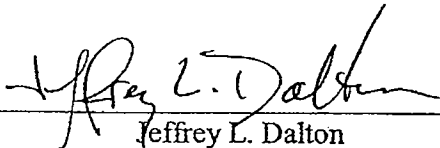
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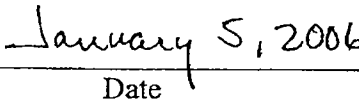
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\_\_\_\_\_  
Jeffrey L. Dalton

  
\_\_\_\_\_  
Date

# Exhibit 3

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re U.S. Patent No.: 6,595,873

Inventor: Michael J. SULLIVAN

Issued: July 22, 2003

Appl. 09/776,278

Filed: February 2, 2001

Titled: MULTI-LAYER GOLF BALL

**REQUEST FOR REEXAMINATION  
UNDER 35 U.S.C. §§ 301-307, 314 AND  
37 C.F.R. §§1.913-1.914**

### DECLARATION OF JEFFREY L. DALTON UNDER 37 C.F.R. § 1.132

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\*\*Polamine 250 is polytetramethyleneoxide-di-p-aminobenzoate having a molecular weight of about 476 g/m.

Rule 132 Declaration of Jeffery L. Dalton

Submitted in Support of Acushnet's request for *Inter Partes* Reexamination of U.S. Patent No. 6,595,873

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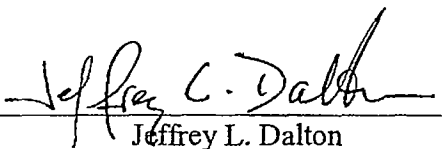
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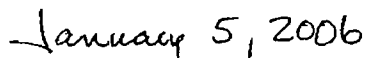
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Jeffrey L. Dalton

  
Date

# Exhibit 4

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re U.S. Patent No.: 6,503,156

Inventor: Michael J. SULLIVAN

Issued: January 7, 2003

Appl. 09/873,642

Filed: June 4, 2001

**Titled: GOLF BALL HAVING MULTI-LAYER  
COVER WITH UNIQUE OUTER  
COVER CHARACTERISTICS**

**REQUEST FOR REEXAMINATION  
UNDER 35 U.S.C. §§ 301-307, 314 AND  
37 C.F.R. §§1.913-1.914**

**DECLARATION OF JEFFREY L. DALTON UNDER 37 C.F.R. § 1.132**

I, Jeffrey L. Dalton, Vice President of Product Development at the Acushnet Company Fairhaven, Massachusetts, hereby declare as follows:

1. I am employed Acushnet Company, located at 333 Bridge Street, Fairhaven, Massachusetts 02719.
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3. I am familiar with the polyurethane material that is described in Example 1 of United States Patent No. 5,334,673 to Shenshen Wu ("Wu"). This composition is reproduced below:

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White Dispersion	5.21

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\*\*Polamine 250 is polytetramethyleneoxide-di-p-aminobenzoate having a molecular weight of about 476 g/m.

Rule 132 Declaration of Jeffery L. Dalton  
Submitted in Support of Acushnet's request for *Inter Partes* Reexamination of U.S. Patent No. 6,503,156

Page 2

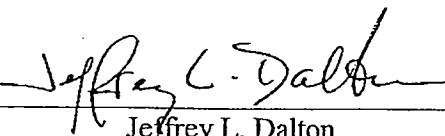
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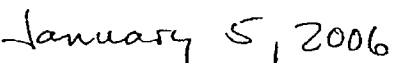
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\_\_\_\_\_  
Jeffrey L. Dalton

  
\_\_\_\_\_  
Date

# Exhibit 5

**REDACTED**  
**IN ITS ENTIRETY**

# Exhibit 6

**REDACTED**  
**IN ITS ENTIRETY**

# Exhibit 7

**REDACTED**  
**IN ITS ENTIRETY**

# Exhibit 8

**REDACTED**  
**IN ITS ENTIRETY**

# Exhibit 9



US005492972A

**United States Patent** [19]

Stefani

[11] Patent Number: **5,492,972**[45] Date of Patent: **Feb. 20, 1996**[54] **GOLF BALL COVER**[75] Inventor: **Barbara Stefani, New Bedford, Mass.**[73] Assignee: **Acushnet Company, Fairhaven, Mass.**

3,819,768	6/1974	Molitor	
4,526,375	7/1985	Nakade	
4,884,814	12/1989	Sullivan	
4,911,451	3/1990	Sullivan et al.	
5,000,459	3/1991	Isaac	525/201
5,328,959	7/1994	Sullivan	

[21] Appl. No.: **56,046**[22] Filed: **Apr. 30, 1993****FOREIGN PATENT DOCUMENTS**

0443706A2	8/1991	European Pat. Off.
0490619A1	6/1992	European Pat. Off.
2105595	8/1982	United Kingdom

**Related U.S. Application Data**

[63] Continuation-in-part of Ser. No. 625,225, Dec. 10, 1990, abandoned.

[51] Int. Cl.<sup>6</sup> ..... **A63B 37/12; C08K 3/14**[52] U.S. Cl. .... **525/196; 525/221; 525/222; 525/330.2; 525/919; 524/908; 273/235.R; 428/402; 428/403**[58] Field of Search ..... **273/235 R, 62; 428/402, 403; 524/908; 525/201, 196, 221, 222, 330.02, 919**[56] **References Cited****U.S. PATENT DOCUMENTS**

3,264,272	8/1966	Rees
3,454,280	7/1969	Harrison et al.

*Primary Examiner*—James J. Scidlick  
*Assistant Examiner*—Duc Truong  
*Attorney, Agent, or Firm*—Pennic & Edmonds

[57] **ABSTRACT**

A polymer blend and a golf ball employing a cover formed of that composition are disclosed. The polymer blend is made from about 95 to about 50 parts by weight of one or more sodium ionomer resins, one of which has a lower flexural modulus than the other sodium ionomer. About 20 to about 50 parts by weight of a lithium ionomer resin is included in the blend. The ball that employs the cover has excellent spin characteristics.

**24 Claims, No Drawings****CW 00506650**

5,492,972

# 1

## GOLF BALL COVER

This is a continuation-in-part of application Ser. No. 07/625,225, filed Dec. 10, 1990, now abandoned.

### FIELD OF THE INVENTION

This invention relates to golf balls and, more particularly, to golf ball cover compositions comprising blends of one or more sodium ionomer resins and a lithium ionomer resin. Golf balls made with the cover composition of the present invention have been found to have good shear resistance, good initial velocity, and excellent spin rates.

### BACKGROUND OF THE INVENTION

Generally, there are three types of golf balls in the market, namely one-piece, two-piece and wound. One-piece balls are molded from a homogeneous mass of material, while two-piece balls are made by molding a cover about a solid core. Wound balls are made by molding a cover about a wound core. A wound core is prepared by winding thin elastic thread about a center.

Golf ball cores, whether wound or solid, typically measure from 1.4 to 1.6 inches (3.5 to 4.1 cm) in diameter. The cover is molded about the core to form a golf ball having the minimum United States Golf Association (USGA) specified diameter of 1.68 inches (4.3 cm). Typically, the cover has a thickness of about 0.04 inches (0.1 cm).

Conventionally, both two-piece and wound golf balls are made by molding covers about cores in one of two ways: by injection molding fluid cover stock material around a core which is held in a retractable pin mold; or by compression molding preformed half-shells about the core. The preformed half-shells are formed by injecting fluid cover stock material into half-shell molds and solidifying the cover stock material into a half-shell shape.

Balata was the standard cover stock material until the middle 1960's when E. I. DuPont de Nemours and Co. discovered a new species of resins known as ionomer resins. These resins are sold under the trademark SURLYN™ and, to a large extent, have replaced balata as a cover stock material. Chemically, these ionomer resins are a copolymer of an olefin and an alpha, beta ethylenically unsaturated carboxylic acid with 10-90% of the carboxylic acid groups being neutralized by a metal ion. See U.S. Pat. No. 3,264,272. Today, the only commercially available ionomer resins are copolymers of ethylene and methacrylic or acrylic acid. These ionomer resins are distinguished by the type of metal ion, the amount of acid, and the degree of neutralization.

Dunlop Rubber Company obtained the first patent on the use of Surlin for the cover of a golf ball, see U.S. Pat. No. 3,454,280 issued Jul. 8, 1969. Since then, there have been a number of disclosures on the use of these ionomer resins in the cover composition of a golf ball. See, for example, U.S. Pat. No. 3,819,768 issued Jun. 25, 1974; U.S. Pat. No. 4,323,247 issued Apr. 6, 1982; U.S. Pat. No. 4,526,375 issued Jul. 2, 1985; U.S. Pat. No. 4,884,814 issued Dec. 3, 1989; and U.S. Pat. No. 4,911,451 issued Mar. 27, 1990.

In November 1986 DuPont introduced a sodium and zinc ionomer resin having a low flexural modulus and suggested using and blending the same with other ionomer resins for making a golf ball cover. Golf ball covers made from these low flexural modulus ionomer resins have good shear resistance but very low velocity.

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In December of 1986, DuPont introduced a lithium ionomer resin which was a copolymer of ethylene and methacrylic acid. These lithium ionomer resins have a very high flexural modulus, typically about 60,000 psi (415 MPa). DuPont suggested that lithium ionomer resins could be used to produce a golf ball cover which would be more cut resistant and harder than a cover made with either sodium or zinc ionomer resins. DuPont also suggested that a golf ball having a cover made from a lithium ionomer resin would go farther, have a higher coefficient of restitution and be less prone to cutting (i.e., more durable) than a golf ball made from other known ionomer resins such as sodium and zinc ionomer resins and blends thereof. DuPont further suggested that lithium ionomer resins could be used in blends with other ionomer resins where they can impart better cut resistance to those other resins.

The United States Golf Association (USGA) has promulgated a rule that no golf ball shall have an initial velocity that exceeds 255 feet (78 m) per second, i.e., 250 feet (76 m) per second with a 2% tolerance. Golf balls with covers made from ionomer resins with low flexural modulus are woefully below this maximum and, as should be appreciated, all golf ball manufacturers strive to come as close as possible to this limit.

For many years, the ball of choice among advanced amateur players and tour professionals has been the balata covered wound ball. This ball is favored because it achieves spin rates sufficient to enable the player to more precisely control ball direction and distance, particularly on shorter approach shots. Balata covered wound balls, however, are expensive.

In order to approximate the characteristics of balata covered wound balls at lower cost, the art has developed two piece balls of varying cover compositions. Despite numerous attempts to replicate the performance of balata covered wound balls, two piece balls generally suffer from low spin rates which makes them difficult to control near the greens. Also, two piece balls tend to have relatively poor click and feel.

A need therefore exists for a two piece ball which has spin rates approximating those of balata covered wound balls.

### SUMMARY OF THE INVENTION

It has now been discovered that in a first embodiment of the invention that the initial velocity of a golf ball which uses a sodium ionomer resin having a low flexural modulus in the cover stock is increased by adding a lithium ionomer resin to the cover stock. It also has been discovered that in a second embodiment of the invention that the spin rate of a two-piece golf ball which uses a cover formed of a blend of one or more sodium ionomers and a lithium ionomer approaches that of a wound balata ball.

Broadly, and in the first embodiment of the invention, the golf ball cover composition is a blend comprising 95 to 50 parts by weight based on 100 parts by weight resin (phr) of a low flexural modulus sodium ionomer resin; and 5 to about 50 phr of a lithium ionomer resin. Preferably, the amount of low flexural modulus sodium ionomer resin is 90 to about 70 phr, more preferably 85 to 75 phr. Preferably, the amount of lithium ionomer resin is 10 to 30 phr, and more preferred 15 to 25 phr.

The lithium ionomer resin employed in the cover blends of the invention is a copolymer comprising 95 to 80 parts by weight of ethylene and 5 to 20 parts by weight of acrylic or methacrylic acid, based on 100 parts by weight copolymer.

CW 00506651

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Preferably, the lithium ionomer resin has 10% to 90% of the acid groups neutralized by lithium.

Preferably, the sodium ionomer resin employed in the cover blends of the invention is a copolymer comprising 95 to 80 parts by weight of copolymer of ethylene and 5 to 20 parts by weight of the copolymer of acrylic or methacrylic acid in which 10% to 90% of the acid groups are neutralized by sodium.

Alternatively, the sodium ionomer is a terpolymer comprising 5-50 weight percent of a softening comonomer such as n- or iso-butyl acrylate, 4-30 weight percent of either acrylic acid or methacrylic acid in which 5-95 percent of the acid groups are neutralized by sodium, and the remainder is ethylene comonomer.

Preferably, the lithium ionomer resin employed in the cover blends of the invention has a very high flexural modulus which is above about 60,000 psi (415 MPa). More preferably, the lithium ionomer resin used in the present invention has a flexural modulus between about 60,000 and about 80,000 psi (415 and 550 MPa). Good results have been obtained with lithium ionomer resins having flexural moduli in the range of about 60,000 psi to about 70,000 psi (415 to 485 MPa). The flexural modulus is measured in accordance with A.S.T.M. Method D-790.

Preferably, the sodium ionomer resins used in the present invention have flexural moduli between 1,000 and 20,000 psi (5 and 140 MPa), more preferably, between 2,000 and 10,000 psi (10 to 70 MPa).

Both the lithium and sodium ionomer resins preferably have 10% to 90% of their carboxylic acid groups neutralized by their respective metal ions. More preferably, both the lithium and sodium ionomer resins have their carboxylic acid groups neutralized by 35% to 65% by the metal ion.

Preferably, the lithium and sodium ionomer resins have the same monocarboxylic acid, e.g. either methacrylic or acrylic acid.

In accordance with the invention, a polymer composition comprising a blend of a lithium ionomer with one or more of a first sodium ionomer and a second sodium ionomer is provided. The lithium ionomer is a copolymer comprising 95 to 80 parts by weight of ethylene and 5 to 20 parts by weight of acrylic or methacrylic acid, based on 100 parts by weight copolymer. The lithium ionomer preferably has a flexural modulus of 61,000 psi. The lithium ionomer can be 45-85 phr, preferably 50-75 phr, most preferably 50 phr of the composition.

In the polymer compositions of the invention, the first sodium ionomer preferably has a flexural modulus of nearly one tenth of the flexural modulus of the second sodium ionomer. The first sodium ionomer, however, is present in a greater amount than the second sodium ionomer. The first sodium ionomer can be 10-75 phr, preferably 45-75 phr, most preferably 45 phr of the composition, and the second sodium ionomer may be 0-15 phr, preferably 4-15 phr, most preferably 5 phr of the composition.

A golf ball having a cover comprising the polymer compositions described above also is provided.

Having briefly summarized the invention, the invention will now be described in detail by reference to the following specification and non-limiting examples. Unless otherwise specified, all temperatures are in degrees Celsius.

#### DETAILED DESCRIPTION OF THE INVENTION

To aid in the processing of fluid cover stock, it is conventional to use a plurality of ionomer resins to obtain the

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desired characteristics. Conventionally, ionomer resins with different melt flow indexes are employed to obtain the desired characteristics of the fluid cover stock. In order to adjust the characteristics of the fluid cover stock, other ionomer resins besides sodium and lithium can be employed.

Good results have been obtained with lithium ionomer resins sold under the trade name SURLYN 8118, 7930 and 7940 by DuPont. Sodium ionomer resins sold by DuPont under the name SURLYN 8269, SURLYN 8320, SURLYN 8265, SURLYN 8120, and SURLYN 8660 also work well in the present invention.

SURLYN 8118, 7930 and 7940 have flexural moduli of 61,000, 67,000 and 61,000 psi (420, 460 and 420 MPa) respectively. SURLYN 8269 and SURLYN 8320 each have a flexural modulus of 2,800 psi (20 MPa). SURLYN 8265 and SURLYN 8120 each have a flexural modulus of 7,100 psi (50 MPa), respectively. SURLYN 8660 has a flexural modulus 34,000 psi.

SURLYN 8118, 7930 and 7940 have melt flow indexes of about 1.4, 1.8 and 2.6 g/10 min., respectively. SURLYN 8269, SURLYN 8320, SURLYN 8265 and SURLYN 8120 each have a melt flow index of about 0.9 g/10 min. SURLYN 8660 has a melt flow index of 10 gm/10 min. Melt flow index is measured in accordance with A.S.T.M. Test D 1238, condition E, procedure A. Preferably, the blend of ionomer resins used to make a cover of a golf ball in accordance with the present invention has a melt flow index between about 1 to about 4 g/10 min., more preferably about 1 to about 3 g/10 min.

The combined amount of lithium ionomer resin and sodium ionomer resin used to make a cover in accordance with the present invention as herein described generally makes up at least about 90% by weight of the total weight of the golf ball cover and, preferably, at least about 95% by weight. Additional materials which may be included in the golf ball cover are other SURLYN resins; other resins such as polybutadiene, polyurethane and polyisoprene; whitening agents such as titanium dioxide; dyes; UV absorbers; optical brighteners; and other additives which are conventionally included in golf ball covers.

The golf ball covers made in accordance with the present invention are made in a conventional manner by molding cover stock formed of the ionomer blends about a core. Molding is accomplished either by injection molding cover stock about a core or by compression molding preformed half-shells of the cover stock about a core. The preferred method is compression molding. Half-shells are made by injection molding a cover stock into a conventional half-shell mold in conventional manner at about 450° F. for about 40 seconds.

The preformed half-shells are then placed about a core and the assembly is introduced into a compression molding machine. The compression molding machine is a hydraulic press having an upper and lower mold plate. As taught by U.S. Pat. No. 4,508,309, such mold plate has half molds, each of which is registered with another half mold in the opposite mold plate. It has been found that a golf ball is formed with a cover in accordance with the present invention when the half-shells are compression molded about a core at about 260° F.-300° F. for about 3 minutes. The molded balls are then cooled while still in the mold and removed when the cover is hard enough to be handled without deforming.

After the balls have been molded, they undergo various conventional finishing operations such as buffing, painting and stamping.

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Preferably, the cover stock used to make golf ball covers in accordance with the present invention is a blend of lithium ionomer resin and at least one sodium ionomer resin in the amounts specified hereinabove. Blending of the ionomer resins is accomplished in a conventional manner using conventional equipment. Good results have been obtained by mixing the ionomer resins in a solid, pelletized form and then placing the mix into a hopper which is used to feed the heated barrel of the injection molding machine. Further mixing is accomplished by a screw in the heated barrel. The injection molding machine is used either to make preformed half-shells for compression molding about a core or for molding flowable cover stock about a core using a retractable-pin mold. Such machines are conventional.

These and other aspects of the present invention may be more fully understood by reference to the following examples.

## EXAMPLE 1

This example compares a series of golf balls made in accordance with the present invention and a series of golf balls having a cover made from a cover stock using only lithium ionomer resin or sodium ionomer resin. The following ingredients are mixed to make cover stocks:

TABLE 1

INGREDIENTS	Cover Stock (Amounts phr)					
	A	B	C	D	E	F
Surlyn 8118 (Lithium)	25	25	20	15	—	100
Surlyn 8269 (Sodium)	25	—	—	—	—	—
Surlyn 8265 (Sodium)	50	75	80	85	100	—
Blue-White Concentrate <sup>1</sup> Containing TiO <sub>2</sub>	5	5	5	5	5	5

<sup>1</sup>From Quantum Chemical Co.

The cover stocks were used to make half-shells in a conventional half-shell injection molding machine which heats the cover stock to 232° C. and injects the fluid cover stock into molds. The half-shells were formed about the solid cores in a compression mold at 127°–138° C. for 10 minutes to yield golf balls with diameters of about 1.68 inches (4.3 cm) and nominal cover thicknesses of about 0.04 inches (0.1 cm).

Each series of balls made from the cover stocks were tested for initial velocity, hardness and cut resistance. The results from these tests were as follows:

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TABLE 2

	A	B	C	D	E	F
Initial Velocity						
(ft/sec)	247.45	247.54	247.26	247.02	246.41	251.32
(m/sec)	75.42	75.45	75.36	75.29	75.11	76.60
Shore D Hardness	54	58	56	55	50	69
Cut Resistance						
(inches)	23	23	23	22	21	29
(cm)	8	8	8	56	53	74

These balls also were tested for shear resistance by projecting the ball against the club face of a Titleist DTR 5-Iron. The angle of impact of the ball on the club face is 50 degrees. Then, the amount of wear on the cover is visually observed. From this visual inspection it was noted that the ball made with cover stock E had the highest shear resistance while the ball made from cover stock F had the lowest. The balls made from cover stocks A–D showed good shear resistance which approached the shear resistance of the ball made from cover stock E.

In the guillotine test, a knife edge of 8 pounds (3629 grams) was impacted against the golf ball from various heights under the force of gravity. Cut resistance was determined by the maximum height to which the knife blade could be raised without cutting the cover of the golf ball on impact. A cut was defined as penetration completely through the cover; a mere crease in the golf ball was not considered to be a cut for testing purposes. The higher the blade had to be raised to cut the cover, the more cut resistant the golf ball was.

Shore D hardness is measured in accordance with A.S.T.M. D 2240-86 durometer hardness. Initial velocity is measured in a conventional manner.

In accordance with the second embodiment of the invention, golf balls employing covers formed from blends of one or more sodium ionomers, preferably two sodium ionomers and a lithium ionomer are produced. Preferably, the sodium ionomers have very large differences in melt flow indices and flexural moduli. The sodium ionomers may be from 15–80 phr, preferably 50 phr of the composition. The lithium ionomer may be 20–80 phr of the composition, preferably 50 phr. Surlyn 8320 may be 10–50 phr, preferably 20–45 phr, most preferably 45 phr of the cover composition; Surlyn 8660 may be 0–10 phr, preferably 5 phr; and Surlyn 7940 may be 45–85 phr, preferably 50–75 phr, most preferably 50 phr by weight. Compositions of suitable cover blends in accordance with this embodiment of the invention are given in Examples 2–9 in Table 3.

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TABLE 3

Ingredient	(Amounts - phr)							
	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Surllyn 8320 <sup>1</sup>	45	10	15	20	25	30	50	75
Surllyn 8660 <sup>2</sup>	5	5	5	5	5	5	5	5
Surllyn 7940 <sup>3</sup>	50	85	80	75	70	65	45	20

<sup>1</sup>Sodium based ionomer from E. I. DuPont de Nemours Co.<sup>2</sup>Sodium based ionomer from E. I. DuPont de Nemours Co.<sup>3</sup>Lithium based ionomer from E. I. DuPont de Nemours Co.

In accordance with the invention, it was found that balls using the cover blends of Examples 2-9 have spin rates intermediate between those of balata covered, wound balls and conventional two piece balls. Moreover, balls which employ covers formed of these terpolymers have click and feel superior to that of conventional two piece balls. The results are shown in Table 4.

TABLE 4

Example No.	2	3	4	5	6	7	8	9
Spin Rate <sup>1</sup>	3403	3300	3300	3300	3300	3300	3400	3600

<sup>1</sup>Spin rate is determined by using a True Temper machine equipped with a driver set up to match U.S.G.A. Standard launch conditions.

By comparison, the spin rates of balata covered wound balls (Titleist Tour 100) is 3800 and a conventional two piece ball (Titleist HVC) is 3000.

Moreover, it is evident from Table 2 that golf ball covers of the present invention produce a faster ball and a more cut resistant ball than covers formed of soft sodium ionomer resin alone.

It will be understood that each and every numerical value which appears in the claims herein is modified by the term "about" if the modifying term "about" does not appear in front of such numerical value.

It will be understood that the claims are intended to cover all changes and modifications of the preferred embodiments of the invention, herein chosen for the purpose of illustration, which do not constitute a departure from the spirit and scope of the invention.

What is claimed is:

1. A polymer composition comprising a blend of a lithium ionomer in an amount of from about 10 to about 30 parts by weight wherein the lithium ionomer has a flexural modulus of between about 60,000 and about 80,000 psi with one or more sodium ionomers in an amount of from about 90 to about 70 parts by weight, wherein at least one of said sodium ionomers is a terpolymer having butyl acrylate therein and having a flexural modulus of between about 1,000 and 20,000 psi.

2. The polymer composition of claim 1 wherein the lithium ionomer is a copolymer comprising from about 95 to 80 parts by weight of ethylene and from about 5 to 20 parts by weight of acrylic or methacrylic acid, based on 100 parts by weight of the copolymer.

3. The polymer composition of claim 2 wherein the lithium ionomer has a flex modulus of about 61,000 psi.

4. The polymer composition of claim 1 wherein the lithium ionomer is about 45-85 phr by weight of said composition.

5. The polymer composition of claim 1 wherein the lithium ionomer is about 50-75 phr of said composition.

6. The polymer composition of claim 1 wherein the lithium ionomer is about 50 phr of said composition.

7. The polymer composition of claim 1 wherein a first sodium ionomer constitutes 45 phr of the composition and a second sodium ionomer constitutes 5 phr of the composition.

8. A golf ball having a cover composition comprising a blend of a lithium ionomer with a first sodium ionomer and a second sodium ionomer,

wherein the lithium ionomer is present in an amount of from about 10 to to about 30 phr wherein the lithium ionomer has a flexural modulus of from about 60,000 to about 80,000 psi, and

the first sodium ionomer and the second sodium ionomer are present in a combined amount of from about 90 to about 70 phr, wherein at least one of the sodium ionomers is a terpolymer having butyl acrylate therein and having a flex modulus of from about 1,000 to about 20,000 psi.

9. The golf ball of claim 8 wherein the first sodium ionomer is a terpolymer.

10. The golf ball of claim 9 wherein the terpolymer is about 5-50 weight percent of a softening comonomer of any of n- or iso-butyl acrylate, 4-30 weight percent of either acrylic acid or methacrylic acid in which 5-95 percent of the acid groups are neutralized by sodium, and the remainder is ethylene comonomer.

11. The golf ball of claim 8 wherein said lithium ionomer is a copolymer comprising about 95 to 80 parts by weight of ethylene and about 5 to 20 parts by weight of acrylic or methacrylic acid, based on 100 parts by weight copolymer.

12. The golf ball of claim 8 wherein said lithium ionomer is 45-85 phr by weight of said composition.

13. The golf ball of claim 8 wherein said lithium ionomer is 50-75 phr of said composition.

14. The golf ball of claim 8 wherein said lithium ionomer is 50 phr of said composition.

15. The golf ball of claim 8 wherein said first sodium ionomer has flexural modulus of about one tenth of the flexural modulus of said second sodium ionomer.

16. The golf ball of claim 8 wherein said first sodium ionomer is present in a greater amount than said second sodium ionomer.

17. The golf ball of claim 8 wherein said first sodium ionomer is 20-45 phr of said composition, and said second sodium ionomer is 15 phr of said composition.

18. The golf ball of claim 8 wherein said lithium ionomer is a copolymer comprising about 95 to 80 parts by weight of ethylene and about 5 to 20 parts by weight of acrylic or methacrylic acid, based on 100 parts by weight copolymer.

19. The golf ball of claim 8 wherein the total parts by weight of said lithium ionomer is 45-85 phr by weight of said composition.

20. The golf ball of claim 8 wherein the total parts by weight of said lithium ionomer is 50-75 phr of said composition.

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21. A polymer composition comprising a blend of a from 10 to 30 parts by weight lithium ionomer with 90 to 70 parts by weight of a first sodium ionomer and a second sodium ionomer, wherein said first sodium ionomer has a flexural modulus of about one tenth of the flexural modulus of said second sodium ionomer.

22. The polymer composition of claim 21 wherein said first sodium ionomer is a terpolymer.

23. The polymer composition of claim 21 where said terpolymer is about 5-50 weight percent of a softening

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comonomer of any of n- or iso-butyl acrylate, 4-30 weight percent of either acrylic acid or methacrylic acid in which 5-95 percent of the acid groups are neutralized by sodium, and the remainder is ethylene comonomer.

24. The polymer composition of claim 21 wherein said first sodium ionomer is present in a greater amount than said second sodium ionomer.

\* \* \* \* \*

# Exhibit 10



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(12) **United States Patent**  
Jordan et al.

(10) Patent No.: **US 6,634,964 B2**  
(45) Date of Patent: **Oct. 21, 2003**

(54) **INITIAL VELOCITY DUAL CORE GOLF BALL**

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(51) Int. Cl.<sup>7</sup> ..... **A63B 37/04; A63B 37/06; A63B 37/00; A63B 37/08**

(52) U.S. Cl. .... **473/377; 473/371; 473/351; 473/367**

(58) Field of Search ..... **473/351-377**

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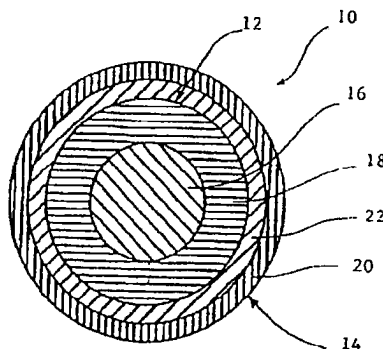
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(57) **ABSTRACT**

A golf ball comprising a core and a cover layer, wherein the core has an outer diameter of no greater than about 1.62 inches; the cover layer comprises an inner cover layer and an outer cover layer having a material hardness of less than about 60 Shore D; and at least one of the core or the cover comprises high-Mooney-viscosity rubber, high-Mooney-viscosity rubber regrind, or a mixture thereof.

**20 Claims, 1 Drawing Sheet**



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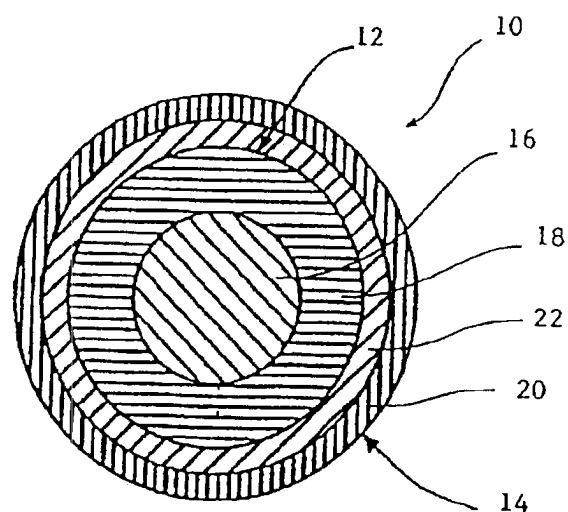
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Oct. 21, 2003

US 6,634,964 B2



**FIG. 1**

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# INITIAL VELOCITY DUAL CORE GOLF BALL

## CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of co-pending U.S. application Ser. No. 09/782,782, filed Feb. 13, 2001, which is a continuation-in-part of co-pending application Ser. No. 09/274,015, filed Mar. 22, 1999, which is a continuation-in-part of U.S. application Ser. No. 08/863,788, filed May 27, 1997, now U.S. Pat. No. 5,885,172, and a continuation-in-part of co-pending application Ser. No. 09/721,740, filed Nov. 27, 2000, which is a continuation-in-part of co-pending application Ser. No. 09/311,591, filed May 14, 1999 now U.S. Pat. No. 6,210,294, and application Ser. No. 09/461,736, filed Dec. 16, 1999, each of which is incorporated herein in its entirety by reference.

## FIELD OF THE INVENTION

This invention relates generally to golf balls, and more specifically, to multilayer golf balls. In particular, this invention relates to a golf ball having at least one core or cover layer comprising high-Mooney-viscosity regrind.

## BACKGROUND OF THE INVENTION

There are a variety of different types of golf ball constructions, the majority of which, however, fall into two general categories: solid and wound golf balls. Solid golf balls include one-piece, two-piece, and multi-layer golf balls. One-piece golf balls are inexpensive and easy to construct, but have poor playing characteristics and are, therefore, usually limited for use as range balls. Two-piece balls are generally constructed with a polybutadiene solid core and a cover and are typically the most popular with recreational golfers because they are very durable and provide good distance. These balls are also relatively inexpensive and easy to manufacture, but are regarded by top players as having limited playing characteristics. Multi-layer golf balls are comprised of a solid core and a cover, either of which may be formed of one or more layers. These balls are regarded as having an extended range of playing characteristics, but are more expensive and difficult to manufacture than are one- and two-piece golf balls.

Wound golf balls, which typically include a fluid-filled center surrounded by tensioned elastomeric material and a cover, generally provide higher spin and soft "feel" characteristics but are more difficult and expensive to manufacture than are one-piece, two-piece, and multi-layer golf balls. Manufacturers are, therefore, constantly striving to produce a solid ball that incorporates the beneficial characteristics of a wound construction.

A variety of golf balls have been designed by manufacturers to provide a wide range of playing characteristics, such as compression, velocity, "feel," and spin. These characteristics can be adjusted and optimized for a variety of playing abilities. For example, manufacturers can adjust these properties by altering the materials (i.e., polymer compositions) and/or the physical construction of each or all of the various golf ball components (i.e., centers, cores, intermediate layers, and covers). Polymers commonly employed by manufacturers for the construction of golf balls include polybutadiene (cores), ionomers, such as SURLYN®, commercially available from DuPont (covers and intermediate layers), and polyurethanes (covers and intermediate layers). Finding the right combination of core

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and layer materials and construction to produce a golf ball suited for a predetermined set of performance criteria, in particular, increased resilience and, therefore, velocity, without a loss in "feel" is a task that is challenging.

It is desirable, therefore, to construct a ball having a soft, thin, urethane cover layer a harder, thin, ionomer inner cover layer, coupled with a polybutadiene center and an outer core layer, at least one of which contains high-Mooney-viscosity regrind, balata, or both. The present invention describes a variety of compositions and constructions employing high-Mooney-viscosity and balata, particularly in center and core layers, for increasing resiliency and improving processing of the material.

## SUMMARY OF THE INVENTION

The present invention is directed to a golf ball comprising a core and a cover layer, wherein the core has an outer diameter of no greater than about 1.62 inches; the cover layer comprises an inner cover layer and an outer cover layer having a material hardness of less than about 60 Shore D; and at least one of the core or the cover includes high-Mooney-viscosity rubber, high-Mooney-viscosity rubber regrind, or a mixture thereof.

In one embodiment, the core comprises a center and at least one outer core layer. The high-Mooney-viscosity rubber or regrind should have a Mooney viscosity of between about 40 and about 80 and, preferably, between about 45 and about 60.

The high-Mooney-viscosity rubber regrind is present in an amount of no greater than about 20 weight percent of the total polymer composition and, more preferably, between about 5 weight percent and about 20 weight percent and, most preferably, in an amount of between about 8 weight percent and about 16 weight percent.

The core outer diameter is from 1.4 inches to about 1.62 inches and, in another embodiment, the outer core layer has an outer diameter from about 1.4 inches to about 1.62 inches. At least one of the cover layers comprises a polyurethane composition comprising the reaction product of at least one polyisocyanate, a polyol, and at least one curing agent and, additionally, at least one of the center or the outer core layer comprise high-Mooney-viscosity rubber regrind. In a preferred embodiment, the outer core layer comprises high-Mooney-viscosity rubber regrind.

The inner cover layer has a material hardness less than about 72 Shore D and, preferably, less than about 68 Shore D. At least one of the inner or outer cover layers includes ionic copolymers of ethylene and an unsaturated monocarboxylic acid; vinyl resins; polyolefins; polyurethanes; polyureas; polyamides; thermoplastic and thermoset resins; metallocenes; acrylic resins; thermoplastic polyesters; nonionic copolymers and terpolymers; or a mixture thereof.

At least one of the core or cover layers are cast, reaction injection molded, liquid injection molded, injection molded, or a combination thereof. In an alternative embodiment, the core has a moment of inertia of less than about 83 and a center deflection of greater than about 4.5 mm under a load of 100 Kg. The outer cover layer also can have a material hardness of less than about 58.

The present invention is also directed to a golf ball comprising a core and a cover layer, wherein the core comprises a solid center and an outer core layer and has an outer diameter of less than about 1.62 inches; the cover layer comprises an inner cover layer and an outer cover layer, the outer cover having a material hardness of no greater than about 58 Shore D; and wherein at least one of the core or

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outer core layer comprises a mold assisting blend including high-Mooney-viscosity rubber, high-Mooney-viscosity rubber regrind, and balata.

The present invention is further directed to a golf ball comprising a core and a cover layer, wherein the core comprises a solid center and an outer core layer and has an outer diameter of between about 1.4 and about 1.62 inches; the cover layer comprises an inner cover layer and an outer cover layer, the outer cover having a material hardness of no greater than about 58 Shore D, and the inner cover layer has a material hardness of less than about 72; and wherein the outer core layer comprises a mold assisting blend comprising high-Mooney-viscosity rubber, high-Mooney-viscosity rubber regrind, and balata.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a golf ball having a dual cover and a dual core according to the invention.

#### DEFINITIONS

The term "about," as used herein in connection with one or more numbers or numerical ranges, should be understood to refer to all such numbers, including all numbers in a range.

As used herein, "cis-to-trans catalyst" means any component or a combination thereof that will convert at least a portion of cis-polybutadiene isomer to trans-polybutadiene isomer at a given temperature. It should be understood that the combination of the cis-isomer, the trans-isomer, and any vinyl-isomer, measured at any given time, comprises 100 percent of the polybutadiene.

As used herein, the term "active ingredients" is defined as the specific components of a mixture or blend that are essential to the chemical reaction.

As used herein, substituted and unsubstituted "aryl" groups means a hydrocarbon ring bearing a system of conjugated double bonds, typically comprising  $4n+2\pi$  ring electrons, where  $n$  is an integer. Examples of aryl groups include, but are not limited to phenyl, naphthyl, anisyl, tolyl, xylenyl and the like. According to the present invention, aryl also includes heteroaryl groups, e.g., pyrimidine or thiophene. These aryl groups may also be substituted with any number of a variety of functional groups. In addition to the functional groups described herein in connection with carbocyclic groups, functional groups on the aryl groups can include hydroxy and metal salts thereof; mercapto and metal salts thereof; halogen; amino, nitro, cyano, and amido; carboxyl including esters, acids, and metal salts thereof; silyl; acrylates and metal salts thereof; sulfonyl or sulfonamide; and phosphates and phosphites; and a combination thereof.

As used herein, the term "Atti compression" is defined as the deflection of an object or material relative to the deflection of a calibrated spring, as measured with an Atti Compression Gauge, that is commercially available from Atti Engineering Corp. of Union City, N.J. Atti compression is typically used to measure the compression of a golf ball. When the Atti Gauge is used to measure cores having a diameter of less than 1.680 in, it should be understood that a metallic or other suitable shim is used to make the diameter of the measured object 1.680 in. As used herein, substituted and unsubstituted "carbocyclic" means cyclic carbon-containing compounds, including, but not limited to cyclopentyl, cyclohexyl, cycloheptyl, adamantyl, and the like. Such cyclic groups may also contain various substitu-

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ents in which one or more hydrogen atoms has been replaced by a functional group. Such functional groups include those described above, and lower alkyl groups having from 1-28 carbon atoms. The cyclic groups of the invention may further comprise a heteroatom.

As used herein, the term "coefficient of restitution" for golf balls is defined as the ratio of the rebound velocity to the inbound velocity when balls are fired into a rigid plate. The inbound velocity is understood to be 125 ft/s.

As used herein, the terms "Group VIA component" or "Group VIA element" mean a component that includes a sulfur component, a selenium component, or a tellurium component, or a combination thereof.

As used herein, the term "sulfur component" means a component that is elemental sulfur, polymeric sulfur, or a combination thereof. It should be further understood that "elemental sulfur" refers to the ring structure of S<sub>8</sub> and that "polymeric sulfur" is a structure including at least one additional sulfur relative to the elemental sulfur.

As used herein, the term "fluid" includes a liquid, a paste, a gel, a gas, or any combination thereof.

As used herein, the term "molecular weight" is defined as the absolute weight average molecular weight. The molecular weight is determined by the following method: approximately 20 mg of polymer is dissolved in 10 mL of tetrahydrofuran ("THF"), which may take a few days at room temperature depending on the polymer's molecular weight and distribution. One liter of THF is filtered and degassed before being placed in a high-performance liquid chromatography ("HPLC") reservoir. The flow rate of the HPLC is set to 1 mL/min through a Viscogel column. This non-shedding, mixed bed, column model GMHHR-H, which has an ID of 7.8 mm and 300 mm long is available from Viscotek Corp. of Houston, Tex. The THF flow rate is set to 1 mL/min for at least one hour before sample analysis is begun or until stable detector baselines are achieved. During this purging of the column and detector, the internal temperature of the Viscotek TDA Model 300 triple detector should be set to 40° C. This detector is also available from Viscotek Corp. The three detectors (i.e., Refractive Index, Differential Pressure, and Light Scattering) and the column should be brought to thermal equilibrium, and the detectors should be purged and zeroed, to prepare the system for calibration according to the instructions provided with this equipment. A 100-μL aliquot of sample solution can then be injected into the equipment and the molecular weight of each sample can be calculated with the Viscotek's triple detector software. When the molecular weight of the polybutadiene material is measured, a  $dn/dc$  of 0.130 should always be used. It should be understood that this equipment and these methods provide the molecular weight numbers described and claimed herein, and that other equipment or methods will not necessarily provide equivalent values as used herein.

As used herein, the term "multilayer" means at least two layers and includes liquid center balls, wound balls, hollow-center balls, and balls with at least two intermediate layers and/or an inner or outer cover.

As used herein, the term "thermoset" material refers to an irreversible, solid polymer that is the product of the reaction of two or more prepolymer precursor materials.

As used herein, the term "parts per hundred," also known as "phr," is defined as the number of parts by weight of a particular component present in a mixture, relative to 100 parts by weight of the total polymer component. Mathematically, this can be expressed as the weight of an

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ingredient divided by the total weight of the polymer, multiplied by a factor of 100.

As used herein, the term "substantially free" means less than about 5 weight percent, preferably less than about 3 weight percent, more preferably less than about 1 weight percent, and most preferably less than about 0.01 weight percent.

As used herein the term "resilience index" is defined as the difference in loss tangent measured at 10 cpm and 1000 cpm divided by 990 (the frequency span) multiplied by 100,000 (for normalization and unit convenience). The loss tangent is measured using an RPA 2000 manufactured by Alpha Technologies of Akron, Ohio. The RPA 2000 is set to sweep from 2.5 to 1000 cpm at a temperature of 100° C. using an arc of 0.5 degrees. An average of six loss tangent measurements were acquired at each frequency and the average is used in calculation of the resilience index. The computation of resilience index is as follows:

$$\text{Resilience Index} = 100,000 \cdot [(\text{loss tangent@10 cpm}) - (\text{loss tangent@1000 cpm})] / 990$$

#### DETAILED DESCRIPTION OF THE INVENTION

The golf ball cores of the present invention may comprise any of a variety of constructions. For example, the core of the golf ball may comprise a conventional center surrounded by an intermediate mantle or outer core layer disposed between the center and the inner cover layer. The core may be a single layer or may comprise a plurality of layers. The innermost portion of the core may be solid or it may be a liquid filled sphere. As with the core, the intermediate mantle or outer core layer may also comprise a plurality of layers. The core may also comprise a solid or liquid filled center around which many yards of a tensioned elastomeric material are wound.

Referring to FIG. 1, preferably the golf ball 10 of the present invention includes a core 12 and a cover 14 surrounding the core 12. The core 12 preferably comprises a center 16 and an outer core layer 18, and the cover 14 comprises an outer cover layer 20 and an inner cover layer 22.

The materials for solid cores include compositions having a base rubber, a crosslinking agent, a filler, and a co-crosslinking or initiator agent. The base rubber typically includes natural or synthetic rubbers. A preferred base rubber is 1,4-polybutadiene having a cis-structure of at least 40%. Most preferably, the base rubber comprises high-Mooney-viscosity rubber. If desired, the polybutadiene can also be mixed with other elastomers known in the art such as natural rubber, polyisoprene rubber (also known as balata) and/or styrene-butadiene rubber in order to modify the properties of the core.

The crosslinking agent includes a metal salt of an unsaturated fatty acid such as a zinc salt or a magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms such as acrylic or methacrylic acid. Suitable cross linking agents include metal salt diacrylates, dimethacrylates and monomethacrylates wherein the metal is magnesium, calcium, zinc, aluminum, sodium, lithium or nickel.

One embodiment of the present invention relates to a multi-layer golf ball having a core comprising a solid center surrounded by at least one additional solid outer core layer. At least one of the outer core layers is formed of a resilient rubber-based component comprising a high-Mooney-viscosity rubber, and a crosslinking agent present in an

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amount from about 20 to about 40 parts per hundred, from about 30 to about 38 parts per hundred, and most preferably about 37 parts per hundred. It should be understood that the term "parts per hundred" is with reference to the rubber by weight.

The center of the ball is preferably solid having a resilient high-Mooney-viscosity rubber component, and a crosslinking agent present in an amount from about 15 to about 30 parts per hundred of the rubber, preferably in an amount from about 19 to about 25 parts per hundred of the rubber and most preferably having about 20 to 24 parts crosslinking agent per hundred of rubber.

The initiator agent can be any known polymerization initiator which decomposes during the cure cycle. Suitable initiators include peroxide compounds such as dicumyl peroxide, 1,1-di(t-butylperoxy) 3,3,5-trimethyl cyclohexane, a-a bis(t-butylperoxy)disopropylbenzene, 2,5-dimethyl-2,5 di(t-butylperoxy)hexane or di-t-butyl peroxide and mixtures thereof.

As used herein, the term "filler" includes any compound or composition that can be used to vary the density and other properties of the core. Fillers typically include materials such as tungsten, zinc oxide, barium sulfate, silica, calcium carbonate, zinc carbonate regrind (recycled core material ground to 30 mesh particle), high-Mooney-viscosity rubber regrind, and the like.

When regrind, and preferably high-Mooney-viscosity rubber regrind, is used in the cores, centers, and intermediate layers of the golf ball, the regrind is typically present in an amount of no greater than about 20 percent by weight of the total polymer composition, more preferably, between about 5 and about 20 weight percent, and most preferably, between about 8 and about 16 weight percent. Is it most preferred that the high-Mooney-viscosity rubber regrind be used in golf ball centers and core or intermediate layers.

The present invention also relates to multilayer golf balls having a core and a cover, such as a solid, hollow, or fluid-filled center, an outer core layer, and an inner and outer cover layer, disposed about the center. At least one of the center or intermediate layers includes a reaction product that includes a cis-to-trans catalyst, a resilient polymer component having polybutadiene, a free radical source, and optionally, a crosslinking agent, a filler, or both.

The invention also includes a method to convert the cis-isomer of the polybutadiene resilient polymer component to the trans-isomer during a molding cycle and to form a golf ball. A variety of methods and materials have been disclosed in U.S. Pat. No. 6,162,135 and U.S. application Ser. No. 09/461,736, filed Dec. 16, 1999; Ser. No. 09/458,676, filed Dec. 10, 1999; and Ser. No. 09/461,421, filed Dec. 16, 1999, each of which are incorporated herein, in their entirety, by reference. Various combinations of polymers, cis-to-trans catalysts, fillers, crosslinkers, and a source of free radicals, may be used. To obtain a higher resilience and lower compression center or intermediate layer, a high-molecular weight polybutadiene with a cis-isomer content preferably greater than about 90 percent is converted to increase the percentage of trans-isomer content at any point in the golf ball or portion thereof, preferably to increase the percentage throughout substantially all of the golf ball or portion thereof, during the molding cycle. More preferably, the cis-polybutadiene isomer is present in an amount of greater than about 95 percent of the total polybutadiene content. Without wishing to be bound by any particular theory, it is believed that a low amount of 1,2-polybutadiene isomer ("vinyl-polybutadiene") is desired in the initial

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polybutadiene, and the reaction product. Preferably, the vinyl polybutadiene isomer content is less than about 7 percent. More preferably, the vinyl polybutadiene isomer content is less than about 4 percent. Most preferably, the vinyl polybutadiene isomer content is less than about 2 percent. Without wishing to be bound by any particular theory, it is also believed that the resulting mobility of the combined cis- and trans-polybutadiene backbone is responsible for the lower modulus and higher resilience of the reaction product and golf balls including the same.

Crosslinkers are included to increase the hardness of the reaction product. Suitable crosslinking agents include one or more metallic salts of unsaturated fatty acids or monocarboxylic acids, such as zinc, calcium, or magnesium acrylate salts, and the like, and mixtures thereof. Preferred acrylates include zinc acrylate, zinc diacrylate, zinc methacrylate, and zinc dimethacrylate, and mixtures thereof. The crosslinking agent must be present in an amount sufficient to crosslink a portion of the chains of polymers in the resilient polymer component. For example, the desired compression may be obtained by adjusting the amount of crosslinking. This may be achieved, for example, by altering the type and amount of crosslinking agent, a method well-known to those of ordinary skill in the art. The crosslinking agent is typically present in an amount greater than about 10 phr of the polymer component, preferably from about 10 to 40 phr of the polymer component, more preferably from about 10 to 30 phr of the polymer component. When an organosulfur is selected as the cis-to-trans catalyst, zinc diacrylate may be selected as the crosslinking agent and is present in an amount of less than about 40 phr.

Fillers added to one or more portions of the golf ball typically include processing aids or compounds to affect rheological and mixing properties, density-modifying fillers, tear strength, or reinforcement fillers, and the like. The fillers are generally inorganic, and suitable fillers include numerous metals or metal oxides, such as zinc oxide and tin oxide, as well as barium sulfate, zinc sulfate, calcium carbonate, barium carbonate, clay, tungsten, tungsten carbide, an array of silicas, and mixtures thereof. Fillers may also include various foaming agents or blowing agents which may be readily selected by one of ordinary skill in the art. Fillers may include polymeric, ceramic, metal, and glass microspheres may be solid or hollow, and filled or unfilled. Fillers are typically also added to one or more portions of the golf ball to modify the density thereof to conform to uniform golf ball standards. Fillers may also be used to modify the weight of the center or at least one additional layer for specialty balls, e.g., a lower weight ball is preferred for a player having a low swing speed.

The polymers, free-radical initiator, filler(s), and any other materials used in forming either the golf ball center or any portion of the core, in accordance with the invention, may be combined to form a mixture by any type of mixing known to one of ordinary skill in the art. Suitable types of mixing include single pass and multi-pass mixing, and the like. The crosslinking agent, and any other optional additives used to modify the characteristics of the golf ball center or additional layer(s), may similarly be combined by any type of mixing. A single-pass mixing process where ingredients are added sequentially is preferred, as this type of mixing tends to increase efficiency and reduce costs for the process. The preferred mixing cycle is single step wherein the polymer, cis-to-trans catalyst, filler, zinc diacrylate, and peroxide are added sequentially. Suitable mixing equipment is well known to those of ordinary skill in the art, and such equipment may include a Banbury mixer, a two-roll mill, or a twin screw extruder.

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Conventional mixing speeds for combining polymers are typically used, although the speed must be high enough to impart substantially uniform dispersion of the constituents. On the other hand, the speed should not be too high, as high mixing speeds tend to break down the polymers being mixed and particularly may undesirably decrease the molecular weight of the resilient polymer component. The speed should thus be low enough to avoid high shear, which may result in loss of desirably high molecular weight portions of the polymer component. Also, too high a mixing speed may undesirably result in creation of enough heat to initiate the crosslinking before the preforms are shaped and assembled around a core. The mixing temperature depends upon the type of polymer components, and more importantly, on the type of free-radical initiator. For example, when using di(2-1-butyl-peroxyisopropyl)benzene as the free-radical initiator, a mixing temperature of about 80° C. to 125° C., preferably about 88° C. to 110° C., and more preferably about 90° C. to 100° C., is suitable to safely mix the ingredients. Additionally, it is important to maintain a mixing temperature below the peroxide decomposition temperature. For example, if dicumyl peroxide is selected as the peroxide, the temperature should not exceed 200° F. Suitable mixing speeds and temperatures are well-known to those of ordinary skill in the art, or may be readily determined without undue experimentation.

The mixture can be subjected to, e.g., a compression or injection molding process, to obtain solid spheres for the center or hemispherical shells for forming an intermediate layer. The polymer mixture is subjected to a molding cycle in which heat and pressure are applied while the mixture is confined within a mold. The cavity shape depends on the portion of the golf ball being formed. The compression and heat liberates free radicals by decomposing one or more peroxides, which may initiate the cis-to-trans conversion and crosslinking simultaneously. The temperature and duration of the molding cycle are selected based upon the type of peroxide and cis-trans catalyst selected. The molding cycle may have a single step of molding the mixture at a single temperature for a fixed time duration. An example of a single step molding cycle, for a mixture that contains dicumyl peroxide, would hold the polymer mixture at 340° F. for a duration of 15 minutes. The molding cycle may also include a two-step process, in which the polymer mixture is held in the mold at an initial temperature for an initial duration of time, followed by holding at a second, typically higher temperature for a second duration of time. An example of a two-step molding cycle would be holding the mold at 290° F. for 40 minutes, then ramping the mold to 340° F. where it is held for a duration of 20 minutes. In a preferred embodiment of the current invention, a single-step cure cycle is employed. Single-step processes are effective and efficient, reducing the time and cost of a two-step process. The resilient polymer component, polybutadiene, cis-to-trans conversion catalyst, additional polymers, free-radical initiator, filler, and any other materials used in forming either the golf ball center or any portion of the core, in accordance with the invention, may be combined to form a golf ball by an injection molding process, which is also well-known to one of ordinary skill in the art. Although the curing time depends on the various materials selected, a particularly suitable curing time is about 5 to 18 minutes, preferably from about 8 to 15 minutes, and more preferably from about 10 to 12 minutes. Those of ordinary skill in the art will be readily able to adjust the curing time upward or downward based on the particular materials used and the discussion herein.

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The cured resilient polymer component, which contains a greater amount of trans-polybutadiene than the uncured resilient polymer component, is formed into an article having a first hardness at a point in the interior and a surface having a second hardness such that the second hardness differs from the first hardness by greater than 10 percent of the first hardness. Preferably, the article is a sphere and the point is the midpoint of the article. In another embodiment, the second hardness differs from the first by greater than 20 percent of the first hardness. The cured article also has a first amount of trans-polybutadiene at an interior location and a second amount of trans-polybutadiene at a surface location, wherein the first amount is at least about 6 percent less than the second amount, preferably at least about 10 percent less than the second amount, and more preferably at least about 20 percent less than the second amount. The interior location is preferably a midpoint and the article is preferably a sphere. The compression of the core, or portion of the core, of golf balls prepared according to the invention is preferably below about 50, more preferably below about 25.

The cover provides the interface between the ball and a club. Properties that are desirable for the cover are good moldability, high abrasion resistance, high tear strength, high resilience, and good mold release, among others. The cover typically has a thickness to provide sufficient strength, good performance characteristics and durability. The cover preferably has a thickness of less than about 0.1 in, more preferably, less than about 0.05 in, and most preferably, between about 0.02 and about 0.04 in. The invention is particularly directed towards a multilayer golf ball which comprises a core, an inner cover layer, and an outer cover layer. In this embodiment, preferably, at least one of the inner and outer cover layers has a thickness of less than about 0.05 in, more preferably between about 0.02 in and about 0.04 in. Most preferably, the thickness of either layer is about 0.03 in.

When the golf ball of the present invention includes an intermediate layer, such as an inner cover layer, this layer can include any materials known to those of ordinary skill in the art, including thermoplastic and thermosetting materials, but preferably the intermediate layer can include any suitable materials, such as ionic copolymers of ethylene and an unsaturated monocarboxylic acid which are available under the trademark SURLYN® of E. I. DuPont de Nemours & Co., of Wilmington, Del., or IOTEK® or ESCOR® of Exxon. These are copolymers or terpolymers of ethylene and methacrylic acid or acrylic acid partially neutralized with salts of zinc, sodium, lithium, magnesium, potassium, calcium, manganese, nickel or the like, in which the salts are the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially neutralized and might include methacrylic, crotonic, maleic, fumaric or itaconic acid.

This golf ball can likewise include one or more homopolymeric or copolymeric inner cover layer materials, such as:

- (1) Vinyl resins, such as those formed by the polymerization of vinyl chloride, or by the copolymerization of vinyl chloride with vinyl acetate, acrylic esters or vinylidene chloride;
- (2) Polyolefins, such as polyethylene, polypropylene, polybutylene and copolymers such as ethylene methylacrylate, ethylene ethylacrylate, ethylene vinyl acetate, ethylene methacrylic or ethylene acrylic acid or propylene acrylic acid and copolymers and homopoly-

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mers produced using a single-site catalyst or a metallocene catalyst;

- (3) Polyurethanes, such as those prepared from polyols and diisocyanates or polyisocyanates and those disclosed in U.S. Pat. No. 5,334,673;
- (4) Polyureas, such as those disclosed in U.S. Pat. No. 5,484,870;
- (5) Polyamides, such as poly(hexamethylene adipamide) and others prepared from diamines and dibasic acids, as well as those from amino acids such as poly(caprolactam), and blends of polyamides with SURLYN®, polyethylene, ethylene copolymers, ethylpropylene-non-conjugated diene terpolymer, and the like;
- (6) Acrylic resins and blends of these resins with polyvinyl chloride, elastomers, and the like;
- (7) Thermoplastics, such as urethanes; olefinic thermoplastic rubbers, such as blends of polyolefins with ethylene-propylene-non-conjugated diene terpolymer; block copolymers of styrene and butadiene, isoprene or ethylene-butylene rubber; or copoly(ether-amide), such as PEBAX®, sold by ELF Atochem of Philadelphia, Pa.;
- (8) Polyphenylene oxide resins or blends of polyphenylene oxide with high impact polystyrene as sold under the trademark NORYL® by General Electric Company of Pittsfield, Mass.;
- (9) Thermoplastic polyesters, such as polyethylene terephthalate, polybutylene terephthalate, polyethylene terephthalate/glycol modified and elastomers sold under the trademarks HYTREL® by E. I. DuPont de Nemours & Co. of Wilmington, Del., and LOMOD® by General Electric Company of Pittsfield, Mass.;
- (10) Blends and alloys, including polycarbonate with acrylonitrile butadiene styrene, polybutylene terephthalate, polyethylene terephthalate, styrene maleic anhydride, polyethylene, elastomers, and the like, and polyvinyl chloride with acrylonitrile butadiene styrene or ethylene vinyl acetate or other elastomers; and
- (11) Blends of thermoplastic rubbers with polyethylene, propylene, polyacetal, nylon, polyesters, cellulose esters, and the like.

Preferably, the optional intermediate layer includes polymers, such as ethylene, propylene, butene-1 or hexane-1 based homopolymers or copolymers including functional monomers, such as acrylic and methacrylic acid and fully or partially neutralized ionomer resins and their blends, methyl acrylate, methyl methacrylate homopolymers and copolymers, imidized, amino group containing polymers, polycarbonate, reinforced polyamides, polyphenylene oxide, high impact polystyrene, polyether ketone, polysulfone, poly(phenylene sulfide), acrylonitrile-butadiene, acrylic-styrene-acrylonitrile, poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene vinyl alcohol), poly(tetrafluoroethylene) and their copolymers including functional comonomers, and blends thereof. Suitable cover compositions also include a polyether or polyester thermoplastic urethane, a thermoset polyurethane, a low modulus ionomer, such as acid-containing ethylene copolymer ionomers, including E/X/Y terpolymers where E is ethylene, X is an acrylate or methacrylate-based softening comonomer present in about 0 to 50 weight percent and Y is acrylic or methacrylic acid present in about 5 to 35 weight percent. More preferably, in a low spin rate embodiment designed for maximum distance, the acrylic or methacrylic

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acid is present in about 16 to 35 weight percent, making the ionomer a high modulus ionomer. In a higher spin embodiment, the inner cover layer includes an ionomer where an acid is present in about 10 to 15 weight percent and includes a softening comonomer.

The cover may include any of the above material but preferably includes a saturated (aliphatic) or unsaturated polyurethane composition comprising the reaction product of at least one polyisocyanate, polyol, and at least one curing agent.

Any polyisocyanate available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyisocyanates include, but are not limited to, 4,4'-diphenylmethane diisocyanate ("MDI"), polymeric MDI, carbodiimide-modified liquid MDI, 4,4'-dicyclohexylmethane diisocyanate ("H<sub>12</sub>MDI"), p-phenylene diisocyanate ("PPDI"), toluene diisocyanate ("TDI"), 3,3'-dimethyl-4,4'-biphenylene diisocyanate ("TODI"), isophoronediiisocyanate ("IPDI"), hexamethylene diisocyanate ("HDI"), naphthalene diisocyanate ("NDI"), xylene diisocyanate ("XDI"); para-tetramethylxylene diisocyanate ("p-TMXDI"); meta-tetramethylxylene diisocyanate ("m-TMXDI"); ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; cyclohexyl diisocyanate; 1,6-hexamethylene-diisocyanate ("HDI"); dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,4,4-trimethyl-1,6-hexane diisocyanate ("TMDI"), tetracene diisocyanate, naphthalene diisocyanate, anthracene diisocyanate, and mixtures thereof. Polyisocyanates are known to those of ordinary skill in the art as having more than one isocyanate group, e.g., di-, tri-, and tetra-isocyanate. Preferably, the polyisocyanate includes MDI, PPDI, TDI, or a mixture thereof, and more preferably, the polyisocyanate includes MDI. It should be understood that, as used herein, the term MDI includes 4,4'-diphenylmethane diisocyanate, polymeric MDI, carbodiimide-modified liquid MDI, and mixtures thereof and, additionally, that the diisocyanate employed may be "low free monomer," understood by one of ordinary skill in the art to have lower levels of "free" monomer isocyanate groups, typically less than about 0.1% free monomer groups. Examples of "low free monomer" diisocyanates include, but are not limited to Low Free Monomer MDI, Low Free Monomer TDI, and Low Free Monomer PPDI.

The at least one polyisocyanate should have less than about 14% unreacted NCO groups. Preferably, the at least one polyisocyanate has no greater than about 7.5% NCO, and more preferably, less than about 7.0%.

Any polyol available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyols include, but are not limited to, polyether polyols, hydroxy-terminated polybutadiene (including partially/fully hydrogenated derivatives), polyester polyols, polycaprolactone polyols, and polycarbonate polyols. In one preferred embodiment, the polyol includes polyether polyol. Examples include, but are not limited to, polytetramethylene ether glycol ("PTMEG"), polyethylene propylene glycol, polyoxypropylene glycol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds and substituted or unsubstituted aromatic and cyclic groups. Preferably, the polyol of the present invention includes PTMEG.

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In another embodiment, polyester polyols are included in the polyurethane material of the invention. Suitable polyester polyols include, but are not limited to, polyethylene adipate glycol, polybutylene adipate glycol, polyethylene propylene adipate glycol, ortho-phthalate-1,6-hexanediol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

In another embodiment, polycaprolactone polyols are included in the materials of the invention. Suitable polycaprolactone polyols include, but are not limited to, 1,6-hexanediol-initiated polycaprolactone, diethylene glycol initiated polycaprolactone, trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

In yet another embodiment, the polycarbonate polyols are included in the polyurethane material of the invention. Suitable polycarbonates include, but are not limited to, polyphthalate carbonate. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups. In one embodiment, the molecular weight of the polyol is from about 200 to about 4000.

Polyamine curatives are also suitable for use in the polyurethane composition of the invention and have been found to improve cut, shear, and impact resistance of the resultant balls. Preferred polyamine curatives include, but are not limited to, 3,5-dimethylthio-2,4-toluenediamine and isomers thereof; 3,5-diethyltoluene-2,4-diamine and isomers thereof, such as 3,5-diethyltoluene-2,6-diamine; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkyldiamino diphenyl methane; p,p'-methylene dianiline ("MDA"); m-phenylenediamine ("MPDA"); 4,4'-methylene-bis-(2-chloroaniline) ("MOCA"); 4,4'-methylene-bis-(2,6-diethylaniline); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenylmethane; 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); trimethylene glycol di-p-aminobenzoate; and mixtures thereof. Preferably, the curing agent of the present invention includes 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, such as ETHACURE 300, commercially available from Albermarle Corporation of Baton Rouge, La. Suitable polyamine curatives, which include both primary and secondary amines, preferably have molecular weights ranging from about 64 to about 2000.

At least one of a diol, triol, tetraol, or hydroxy-terminated curatives may be added to the aforementioned polyurethane composition. Suitable diol, triol, and tetraol groups include ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy) benzene; 1,3-bis-[2-(2-hydroxy)ethoxy] benzene; 1,3-bis-[2-(2-(2-hydroxyethoxy)ethoxy] ethoxy]benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(β-hydroxyethyl)ether; hydroquinone-di-(β-hydroxyethyl)ether; and mixtures thereof. Preferred hydroxy-terminated curatives include ethylene glycol; diethylene glycol; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol, trimethylol propane, and mixtures thereof. Preferably, the hydroxy-terminated curatives have molecular weights ranging from about 48 to 2000. It

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should be understood that molecular weight, as used herein, is the absolute weight average molecular weight and would be understood as such by one of ordinary skill in the art.

Both the hydroxy-terminated and amine curatives can include one or more saturated, unsaturated, aromatic, and cyclic groups. Additionally, the hydroxy-terminated and amine curatives can include one or more halogen groups. The polyurethane composition can be formed with a blend or mixture of curing agents. If desired, however, the polyurethane composition may be formed with a single curing agent.

Any method known to one of ordinary skill in the art may be used to combine the polyisocyanate, polyol, and curing agent of the present invention. One commonly employed method, known in the art as a one-shot method, involves concurrent mixing of the polyisocyanate, polyol, and curing agent. This method results in a mixture that is inhomogeneous (more random) and affords the manufacturer less control over the molecular structure of the resultant composition. A preferred method of mixing is known as a prepolymer method. In this method, the polyisocyanate and the polyol are mixed separately prior to addition of the curing agent. This method affords a more homogeneous mixture resulting in a more consistent polymer composition.

An optional filler component may be chosen to impart additional density to blends of the previously described components. The selection of such filler(s) is dependent upon the type of golf ball desired (i.e., one-piece, two-piece multi-component, or wound). Examples of useful fillers include zinc oxide, barium sulfate, calcium oxide, calcium carbonate and silica, as well as the other well known corresponding salts and oxides thereof. Additives, such as nanoparticles, glass spheres, and various metals, such as titanium and tungsten, can be added to the polyurethane compositions of the present invention, in amounts as needed, for their well-known purposes. Additional components which can be added to the polyurethane composition include UV stabilizers and other dyes, as well as optical brighteners and fluorescent pigments and dyes. Such additional ingredients may be added in any amounts that will achieve their desired purpose. Due to the very thin nature, it has been found by the present invention that the use of a castable, reactive material, which is applied in a fluid form, makes it possible to obtain very thin outer cover layers on golf balls. Specifically, it has been found that castable, reactive liquids, which react to form a urethane elastomer material, provide desirable very thin outer cover layers.

The castable, reactive liquid employed to form the urethane elastomer material can be applied over the inner core using a variety of application techniques such as spraying, dipping, spin coating, or flow coating methods which are well known in the art. An example of a suitable coating technique is that which is disclosed in U.S. Pat. No. 5,733,428, the disclosure of which is hereby incorporated by reference in its entirety in the present application.

The cover is preferably formed around the inner cover layer by mixing and introducing the material in the mold halves. It is important that the viscosity be measured over time, so that the subsequent steps of filling each mold half, introducing the core into one half and closing the mold can be properly timed for accomplishing centering of the core cover halves fusion and achieving overall uniformity. Suitable viscosity range of the curing urethane mix for introducing cores into the mold halves is determined to be approximately between about 2,000 cP and about 30,000 cP, with the preferred range of about 8,000 cP to about 15,000 cP.

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To start the cover formation, mixing of the prepolymer and curative is accomplished in motorized mixer including mixing head by feeding through lines metered amounts of curative and prepolymer. Top preheated mold halves are filled and placed in fixture units using pins moving into holes in each mold. After the reacting materials have resided in top mold halves for about 40 to about 80 seconds, a core is lowered at a controlled speed into the gelling reacting mixture. At a later time, a bottom mold half or a series of bottom mold halves have similar mixture amounts introduced into the cavity.

A ball cup holds the ball core through reduced pressure (or partial vacuum) in hose. Upon location of the coated core in the halves of the mold after gelling for about 40 to about 80 seconds, the vacuum is released allowing core to be released. The mold halves, with core and solidified cover half thereon, are removed from the centering fixture unit, inverted and mated with other mold halves which, at an appropriate time earlier, have had a selected quantity of reacting polyurethane prepolymer and curing agent introduced therein to commence gelling.

Similarly, U.S. Pat. Nos. 5,006,297 and 5,334,673 both also disclose suitable molding techniques which may be utilized to apply the castable reactive liquids employed in the present invention. Further, U.S. Pat. Nos. 6,180,040 and 6,180,722 disclose methods of preparing dual core golf balls. The disclosures of these patents are hereby incorporated by reference in their entirety. However, the method of the invention is not limited to the use of these techniques.

Depending on the desired properties, balls prepared according to the invention can exhibit substantially the same or higher resilience, or coefficient of restitution ("COR"), with a decrease in compression or modulus, compared to balls of conventional construction. Additionally, balls prepared according to the invention can also exhibit substantially higher resilience, or COR, without an increase in compression, compared to balls of conventional construction. Another measure of this resilience is the "loss tangent," or  $\tan \delta$ , which is obtained when measuring the dynamic stiffness of an object. Loss tangent and terminology relating to such dynamic properties is typically described according to ASTM D4092-90. Thus, a lower loss tangent indicates a higher resiliency, thereby indicating a higher rebound capacity. Low loss tangent indicates that most of the energy imparted to a golf ball from the club is converted to dynamic energy, i.e., launch velocity and resulting longer distance. The rigidity or compressive stiffness of a golf ball may be measured, for example, by the dynamic stiffness. A higher dynamic stiffness indicates a higher compressive stiffness. To produce golf balls having a desirable compressive stiffness, the dynamic stiffness of the crosslinked reaction product material should be less than about 50,000 N/m at  $-50^{\circ}\text{C}$ . Preferably, the dynamic stiffness should be between about 10,000 and 40,000 N/m at  $-50^{\circ}\text{C}$ , more preferably, the dynamic stiffness should be between about 20,000 and 30,000 N/m at  $-50^{\circ}\text{C}$ .

The resultant golf balls typically have a coefficient of restitution of greater than about 0.7, preferably greater than about 0.75, and more preferably greater than about 0.78. The golf balls also typically have an Atti compression of at least about 40, preferably from about 50 to 120, and more preferably from about 60 to 100. The golf ball polybutadiene material of the present invention typically has a flexural modulus of from about 500 psi to 300,000 psi, preferably from about 2000 to 200,000 psi. The golf ball polybutadiene material typically has a hardness of at least about 15 Shore A, preferably between about 30 Shore A and 80 Shore D, more preferably between about 50 Shore A and 60 Shore D.

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The specific gravity of the center composition is typically greater than about 0.7 and preferably greater than about 1.0. The center and the outer core layer may have the same or different specific gravity values. In one embodiment, the center and outer core layer have different specific gravity values. It is preferred, however, that the specific gravity of the outer core layer and the center differ by less than 0.1.

The center composition should comprise at least one rubber material having a resilience index of at least about 40. Preferably the resilience index is at least about 50. Polymers that produce resilient golf balls and, therefore, are suitable for the present invention, include but are not limited to CB23, CB22, BR60, and 1207G. To clarify the method of computation for resilience index, the resilience index for CB23, for example, is computed as follows:

$$\text{Resilience Index for CB23} = 100,000 \{ (0.954) - (0.407) \} / 990$$

$$\text{Resilience Index for CB23} = 55$$

The molding process and composition of golf ball portions typically results in a gradient of material properties. Methods employed in the prior art generally exploit hardness to quantify these gradients. Hardness is a qualitative measure of static modulus and does not represent the modulus of the material at the deformation rates associated with golf ball use, i.e., impact by a club. As is well known to one skilled in the art of polymer science, the time-temperature superposition principle may be used to emulate alternative deformation rates. For golf ball portions including polybutadiene, a 1-Hz oscillation at temperatures between 0° C. and -50° C. are believed to be qualitatively equivalent to golf ball impact rates. Therefore, measurement of loss tangent and dynamic stiffness at 0° C. to -50° C. may be used to accurately anticipate golf ball performance, preferably at temperatures between about -20° C. and -50° C.

Additionally, the unvulcanized rubber, such as polybutadiene, in golf balls prepared according to the invention typically has a Mooney viscosity of between about 40 and about 80, more preferably, between about 45 and about 60, and most preferably, between about 45 and about 55. Mooney viscosity is typically measured according to ASTM D-1646.

When golf balls are prepared according to the invention, they typically will have dimple coverage greater than about 60 percent, preferably greater than about 65 percent, and more preferably greater than about 75 percent. The flexural modulus of the cover on the golf balls, as measured by ASTM method D6272-98, Procedure B, is typically greater than about 500 psi, and is preferably from about 500 psi to 150,000 psi. As discussed herein, the outer cover layer is preferably formed from a relatively soft polyurethane material. In particular, the material of the outer cover layer should have a material hardness, as measured by ASTM-2240, preferably less than about 60 Shore D, more preferably less than about 55 Shore D, and most preferably less than about 50 Shore D. The outer cover layer hardness, as measured on the golf ball, is preferably greater than about 50. The inner cover layer preferably has a material hardness less than 72 Shore D, more preferably less than about 70 Shore D, and most preferably, less than about 68 Shore D. It is preferred that the center, outer core layer, and inner cover layer each have a different hardness and more preferably, that the hardness progressively increases away from the center until reaching the outer cover layer, i.e., the outer core layer is harder than the center and the inner cover layer is harder than the outer core layer.

The overall outer diameter ("OD") of the center is preferably from about 0.375 in to about 1.4 in, more preferably

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from about 0.5 in to about 1.25 in, and most preferably from about 0.9 in to about 1.2 in. The OD of the outer core layer is preferably from about 1.4 in to about 1.62 in, more preferably from about 1.52 in to about 1.59 in, and most preferably from about 1.535 in to about 1.58 in. The OD of the inner cover layer of the golf balls of the present invention is preferably greater than about 1.58 in, more preferably from about 1.59 in to about 1.66 in, and most preferably from about 1.6 in to about 1.64 in.

The present multilayer golf ball can have an overall diameter of any size. Although the United States Golf Association ("USGA") specifications limit the minimum size of a competition golf ball to 1.680 in. There is no specification as to the maximum diameter. Golf balls of any size, however, can be used for recreational play. The preferred diameter of the present golf balls is from about 1.680 in to about 1.800 in. The more preferred diameter is from about 1.680 in to about 1.760 in. The most preferred diameter is about 1.680 in to about 1.740 in.

The golf balls of the present invention should have a moment of inertia ("MOI") of less than about 83 and, preferably, less than about 82. The MOI is typically measured on model number MOI-005-104 Moment of Inertia Instrument manufactured by Inertia Dynamics of Collinsville, Conn. The instrument is plugged into a PC for communication via a COMM port and is driven by MOI Instrument Software version #1.2.

The golf balls of the present invention should have a center deflection of greater than about 4.5 mm under a load of 100 Kg. Preferably, the center deflection is greater than about 4.8 mm and, more preferably, about 5.0 mm under a load of 100 Kg. The deflection data is measured with a Stable Micro Systems, Materials Master, (model number MT-LQ) instrument commercially available from Mono Research Labs. The MT-LQ is equipped with a 500 Kg load cell, which begins measuring deflection when 60 g is placed on it.

Prior to measuring deflection, the platens are calibrated. After calibration, the operator places the sphere to be measured on the surface of the bottom platen. The top platen moves down with a crosshead speed of one in/min. When the surface of the top platen contacts the sphere and reaches a compressive force of 60 g (the trigger force), the displacement is measured as a function of force, with force being the independent variable on the x axis. The instrument measures a predetermined number of data points/min which result in a plot of displacement versus force, from which the displacement of the sphere at a load of 100 Kg can be determined.

#### EXAMPLE

Two golf balls were prepared according to the present invention and are designated VDC45 and VDC48 in Table I below. The VDC golf balls contained a core formed of a 1.0-in-diameter solid center and an outer core layer having a thickness of 0.275 in to form a core having an outer diameter of 1.55 in. The core was surrounded by an inner cover layer having a thickness of 0.035 in and an outer cover layer having a thickness of 0.030 in, to provide a golf ball outer diameter of 1.68 in. A control golf ball was prepared according to conventional technology. The control ball was formed of a solid core having a diameter of 1.550 in, an inner cover layer having a thickness of 0.035 in, and an outer cover layer having a thickness of 0.030 in, to provide a golf ball outer diameter of 1.68 in. The center compositions for both golf balls are presented below in Table I.

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TABLE I

Center Composition	VDC45	VDC48	Control
CB23	100.0	100.0	100.0
zinc diacrylate	25.05	25.05	27.0
zinc oxide	5.26	5.26	4.3
di- <i>t</i> -butyl disulfide	0.63	0.63	—
DCP-70 <sup>1</sup>	2.0	2.0	—
tungsten	33.4	33.4	12.74
color dispersion	0.07	0.07	0.14
Trigonox-265 <sup>2</sup>	—	—	0.53

<sup>1</sup>DCP-70 is dicumyl peroxide on a binder in pellet and is commercially available from Elastchem, Inc. of Chardon, OH

<sup>2</sup>a peroxide mixture on filler commercially available from Akzo Nobel Chemicals Inc. of Chicago, IL

The outer core layer composition for both VDC balls comprises high-Mooney-viscosity CB23 polybutadiene, zinc diacrylate, zinc oxide, DCP-70, Kuraray TP 251, Varox 231XL, and a color dispersion. The inner cover layers were the same construction for both VDC balls and the control ball. The inner cover layers were formed of a 50/50 Na/Li blend of SURLYN® 8945 and SURLYN® 7940. The outer cover layer of the VDC45 ball comprises a PMS1088 prepolymer, commercially available from Polyurethane Specialties Co. (77.8%) cured with Ethacure 300, commercially available from Albemarle Corp. (18.7%), and white dispersion, commercially available from Harwich Chemical (3.5%).

The outer cover layer of the VDC48 ball comprises a Vibrathane B-625 prepolymer, commercially available from Uniroyal (80.5%; NCO level: 6.1–6.6%) cured with Ethacure 300, commercially available from Albemarle Corp. (16%), and white dispersion, commercially available from Harwich Chemical (3.5%).

The VDC balls were formed in two different constructions, one with an outer cover layer having a material Shore D hardness of about 45, and a second with an outer cover layer having a material Shore D hardness of about 48. The VDC balls were tested for a variety of golf ball properties, such as ball compression, center hardness (interior and surface), core layer hardness, inner cover layer hardness, cover hardness, and compared to the Control ball, also tested for the same properties.

TABLE II

Ball Properties	VDC45	VDC48	Control
Ball Compression (Atti)	96	96	85
Center-surface hardness <sup>1</sup> (Shore C)	73.3	73.3	
Outer Core Layer hardness <sup>1</sup> (Shore C)	83.3	83.3	
Inner Cover Layer hardness <sup>1</sup> (Shore D)	62.8	62.8	
Cover hardness <sup>1</sup> (Shore D)	56	58	57
moment of inertia (g · cm <sup>2</sup> )	80.73	80.73	81.11
CoR	0.815	0.817	0.815

<sup>1</sup>hardness measured directly on the golf ball (as compared to material hardness)

The launch angle and spin were measured for both VDC balls and the Control ball, for a variety of golf clubs. The data for each ball, off of each club type, are presented below in Table III.

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TABLE III

	Launch Angle (°)	Spin (rpm)
Club: Pro Driver <sup>1</sup>		
VDC45	9.5	3072
VDC48	9.3	3134
Control	9.2	3357
Club: Standard Driver <sup>2</sup>		
VDC45	9.1	3091
VDC48	9.1	3038
Control	9.0	3370
Club: 8-Iron <sup>3</sup>		
VDC45	19.3	7035
VDC48	19.6	6863
Control	18.9	7457
Club: Wedge <sup>4</sup>		
VDC45	25.5	9335
VDC48	25.5	9290
Control	25.0	9623

<sup>1</sup>Ball Speed: 167; Launch Angle: 9°; Spin Rate: 3500 rpm; Club: Driver; Club Head: 975D; Loft: 7.5°; Shaft: Graphite Design YS9-X

<sup>2</sup>Ball Speed: 160 mph; Launch Angle: 9.5°; Spin Rate: 3000 rpm; Club: Driver; Club Head: 975D; Loft: 8.5°; Shaft: X100

<sup>3</sup>Ball Speed: 115 mph; Launch Angle: 18.5°; Spin Rate: 9000 rpm; Club: 8-iron; Club Head: DCI Black; Loft: 40°; Shaft: X100

<sup>4</sup>Ball Speed: 95; Launch Angle: 24°; Spin Rate: 10400 rpm; Club: wedge; Club Head: DCI Black; Loft: 46°; Shaft: X-100

It is clear from the data presented in Table III, that the golf ball of the present invention decreases driver spin for both a Pro driver and a Standard driver. One of ordinary skill in the art is well aware that decreasing driver spin to optimize flight increases distance off the tee. Too much 8-iron spin can make approach shots into the green difficult to control whereas wedge spin is important to making approach shots stop at desired locations on the green, especially when a player is pitching or chipping to the green.

The invention described and claimed herein is not to be limited in scope by the specific embodiments herein disclosed, since these embodiments are intended as illustrations of several aspects of the invention. Any equivalent embodiments are intended to be within the scope of this invention. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

What is claimed is:

1. A golf ball comprising a core and a cover, wherein:
  - a) the core has an outer diameter of no greater than about 1.62 inches;
  - b) the cover comprises an inner cover layer and an outer cover layer, the outer cover layer having a material hardness of less than about 60 Shore D;
  - c) at least one of the core or the cover comprises a high-Mooney-viscosity rubber regrind, or a mixture of a high-Mooney-viscosity rubber regrind and a high-Mooney-viscosity rubber, the high-Mooney-viscosity rubber regrind being present in an amount of no greater than about 20 weight percent.
2. The golf ball of claim 1, wherein the core comprises a center and at least one outer core layer.
3. The golf ball of claim 2, wherein the outer core layer has an outer diameter from about 1.4 inches to about 1.62 inches.
4. The golf ball of claim 2, wherein the outer core layer comprises high-Mooney-viscosity rubber regrind.

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5. The golf ball of claim 1, wherein at least one of the high-Mooney-viscosity rubber or regrind has a Mooney viscosity of between about 40 and about 80.

6. The golf ball of claim 5, wherein at least one of the high-Mooney-viscosity rubber or regrind has a Mooney viscosity of between about 45 and about 60.

7. The golf ball of claim 1, wherein the high-Mooney-viscosity rubber regrind is present in an amount between about 5 weight percent and about 20 weight percent.

8. The golf ball of claim 7, wherein the high-Mooney-viscosity rubber regrind is present in an amount of between about 8 weight percent and about 16 weight percent.

9. The golf ball of claim 1, wherein the core outer diameter is from 1.4 inches to about 1.62 inches.

10. The golf ball of claim 1, wherein the inner cover layer has a material hardness less than about 72 Shore D.

11. The golf ball of claim 10, wherein the inner cover layer has a material hardness less than about 68 Shore D.

12. The golf ball of claim 1, wherein at least one of the inner or outer cover layers comprises a material selected from the group consisting of ionic copolymers of ethylene and an unsaturated monocarboxylic acid; vinyl resins; polyolefins; polyurethanes; polyureas; polyamides; thermoplastic and thermoset resins; metallocenes; acrylic resins; thermoplastic polyesters; and non-ionic copolymers and terpolymers.

13. The golf ball of claim 1, wherein at least one of the core or cover layers are cast, reaction injection molded, liquid injection molded, injection molded, or a combination thereof.

14. The golf ball of claim 1, wherein the core has a moment of inertia of less than about 83 g-cm<sup>2</sup> and a center deflection of greater than about 4.5 mm under a load of 100 Kg.

15. The golf ball of claim 1, wherein the outer cover layer has a material hardness less than about 58.

16. The golf ball of claim 1, wherein at least one of the cover layers comprises a polyurea composition.

17. A golf ball comprising a core and a cover layer, wherein:

the core comprises a solid center and an outer core layer and has an outer diameter of less than about 1.62 inches;

the cover layer comprises an inner cover layer and an outer cover layer, the outer cover having a material hardness of no greater than about 58 Shore D; and wherein

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at least one of the core or outer core layer comprises a blend of high-Mooney-viscosity rubber, high-Mooney-viscosity rubber regrind, and balata.

18. A golf ball comprising a core and a cover layer, wherein:

the core comprises a solid center comprising high-Mooney-viscosity rubber and an outer core layer, and has an outer diameter of between about 1.4 and about 1.62 inches;

the cover layer comprises an inner cover layer and an outer cover layer, the outer cover having a material hardness of no greater than about 58 Shore D, and the inner cover layer has a material hardness of less than about 72; and wherein

the outer core layer comprises a blend of high-Mooney-viscosity rubber regrind and balata in an amount sufficient to increase the resilience.

19. A golf ball comprising a core and a cover, wherein: the core has an outer diameter of no greater than about 1.62 inches;

the cover comprises an inner cover layer and an outer cover layer, the outer cover layer having a material hardness of less than about 60 Shore D;

at least one of the core or the cover comprises a high-Mooney-viscosity rubber regrind, or a mixture of a high-Mooney-viscosity rubber regrind and a high-Mooney-viscosity rubber; and

at least one of the cover layers comprises a polyurethane composition comprising a reaction product of at least one polyisocyanate, a polyol, and at least one curing agent.

20. A golf ball comprising a core and a cover, wherein: the core has an outer diameter of no greater than about 1.62 inches;

the core comprises a center and at least one outer core layer;

the cover comprises an inner cover layer and an outer cover layer, the outer cover layer having a material hardness of less than about 60 Shore D; and

at least one of the center or the outer core layer comprises a high-Mooney-viscosity rubber regrind, or a mixture of a high-Mooney-viscosity rubber regrind and a high-Mooney-viscosity rubber.

\* \* \* \* \*

# Exhibit 11



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(12) **United States Patent**  
Wu et al.

(10) Patent No.: **US 6,818,705 B2**  
(45) Date of Patent: **Nov. 16, 2004**

(54) **THIN-LAYER-COVERED GOLF BALL WITH IMPROVED VELOCITY**

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(60) Provisional application No. 60/113,949, filed on Dec. 24, 1998.

(51) Int. Cl.<sup>7</sup> ..... A63B 37/12; A63B 37/06

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(58) Field of Search ..... 525/261, 274; 473/373, 374, 377

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(57) **ABSTRACT**

A golf ball comprising a center comprising a polybutadiene having a molecular weight of greater than 200,000 and a resilience index of at least about 40; and a cover layer comprising a polyurethane composition formed from a pre-polymer having no greater than 7.5 percent by weight unreacted isocyanate groups.

22 Claims, 1 Drawing Sheet

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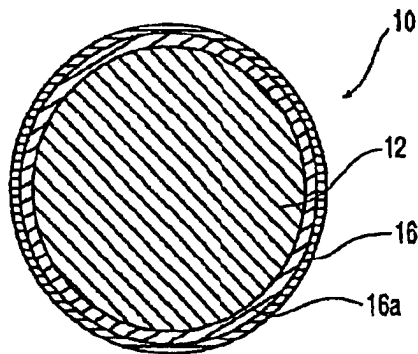
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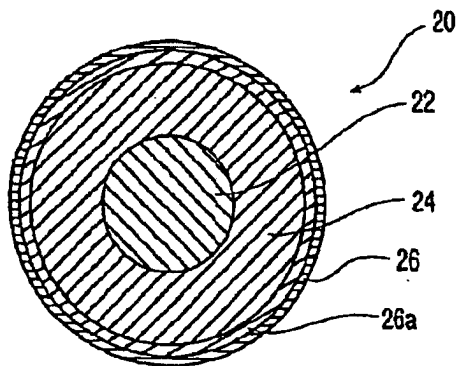
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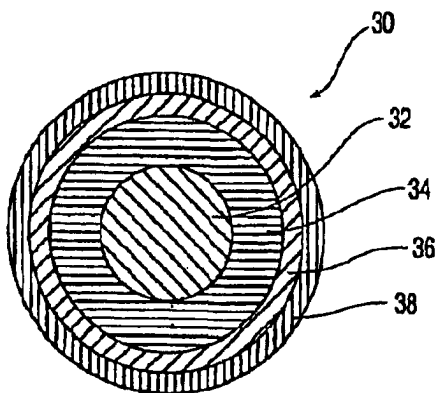
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*Fig. 1*



*Fig. 2*



*Fig. 3*

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# THIN-LAYER-COVERED GOLF BALL WITH IMPROVED VELOCITY

## CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 09/721,740, filed Nov. 27, 2000, now U.S. Pat. No. 6,486,261, which is a continuation-in-part of U.S. patent application Ser. No. 09/461,736, filed Dec. 16, 1999, now U.S. Pat. No. 6,465,578, which claims the benefit of U.S. Patent Provisional Application No. 60/113,949, filed Dec. 24, 1998, and is a continuation-in-part of U.S. patent application Ser. No. 09/311,591, filed May 14, 1999, now U.S. Pat. No. 6,210,294, and also a continuation-in-part of U.S. patent application Ser. No. 09/274,015, filed Mar. 22, 1999.

## FIELD OF THE INVENTION

The invention relates generally to golf balls and, more specifically, to golf balls with covers formed of a polymer blend comprising a polyurethane composition and cores formed of a polybutadiene composition. The polyurethane composition comprises a prepolymer of a polyisocyanate and a polyol, and a diamine curing agent. The polybutadiene composition comprises a butadiene polymer with a resilience index greater than about 40 and a molecular weight greater than about 200,000. The golf balls of the present invention have been found to provide improved velocity.

## BACKGROUND OF THE INVENTION

Conventional golf balls can be divided into several general classes: (a) solid golf balls having one or more layers, and (b) wound golf balls. Solid golf balls include one-piece balls, which are easy to construct and relatively inexpensive, but have poor playing characteristics and are thus generally limited for use as range balls. Two-piece balls are constructed with a generally solid core and a cover and are generally the most popular with recreational golfers because they are very durable and provide maximum distance. Balls having a two-piece construction are commonly formed of a polymeric core encased by a cover. Typically, the core is formed from polybutadiene that is chemically crosslinked with zinc diacrylate and/or other similar crosslinking agents. These balls are generally easy to manufacture, but are regarded as having limited playing characteristics. Solid golf balls also include multi-layer golf balls that are comprised of a solid core of one or more layers and/or a cover of one or more layers. These balls are regarded as having an extended range of playing characteristics.

Wound golf balls are generally preferred by many players due to their high spin and soft "feel" characteristics. Wound golf balls typically include a solid, hollow, or fluid-filled center, surrounded by a tensioned elastomeric material and a cover. Wound balls generally are more difficult and expensive to manufacture than solid two-piece balls.

A variety of golf balls have been designed by manufacturers to provide a wide range of playing characteristics, such as compression, velocity, "feel," and spin. These characteristics can be optimized for various playing abilities. One of the most common components that manufacturers have addresses for optimizing and/or altering the playing characteristics of golf balls, is the polymer components present in modern golf ball construction, in particular, golf ball centers and/or core. In addition to ionomers, one of the most common polymers employed is polybutadiene and, more specifically, polybutadiene having a high cis-isomer concentration.

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The use of a polybutadiene having a high cis-concentration results in a very resilient and rigid golf ball, especially when coupled with a hard cover material. These highly resilient golf balls have a relatively hard "feel" when struck by a club. Soft "feel" golf balls constructed with a high cis-polybutadiene have low resilience. In an effort to provide improved golf balls, various other polybutadiene formulations have been prepared, as discussed below.

U.S. Pat. No. 3,239,228 discloses a solid golf ball having a core molded of polybutadiene rubber with a high sulfur content, and a cover. The polybutadiene content of the core is stereo-controlled to the configuration 25–100 percent cis- and 0–65 percent trans-1,4-polybutadiene, with any remainder having a vinyl configuration of polybutadiene. A preferred embodiment of the polybutadiene golf ball core contains 35 percent cis-, 52 percent trans-, and 13 percent vinyl-polybutadiene. The level of trans- and vinyl-content are disclosed to be unimportant to the overall playing characteristics of the polymer blend.

British Patent No. 1,168,609 discloses a molding composition from which improved golf ball cores can be molded and which contains cis-polybutadiene as a basic polymer component. The core polymer component typically includes at least 60 percent cis-polybutadiene, with the remainder being either the trans- or vinyl-forms of polybutadiene. In a preferred embodiment, the core polybutadiene component contains 90 percent cis-configuration, with the remaining 10 percent being either the trans- or vinyl-configurations of 1,4-polybutadiene.

U.S. Pat. Nos. 3,572,721 and 3,572,722 disclose a solid, one- or two-piece golf ball, with the two-piece ball having a core and a cover. The cover material can include any one of a number of materials, or blends thereof, known to those of ordinary skill in the art, including trans-polybutadiene which may be present in an amount from at least 90 percent, with the remainder being the cis- and/or vinyl configuration.

British Patent No. 1,209,032 discloses a two- or three-piece golf ball having a core and a cover. The core or cover material can be any material capable of being crosslinked. In particular, the material can be a polymer or a copolymer of butadiene or isoprene. Preferably, the polymer component is polybutadiene having a cis content of greater than 50 percent by weight.

U.S. Pat. No. 3,992,014 discloses a one-piece, solid golf ball. The golf ball material is typically polybutadiene, with a stereo-configuration selected to be at least 60 percent cis-polybutadiene, with the remaining 40 percent being the trans-polybutadiene and/or 1,2-polybutadiene (vinyl) isomers.

U.S. Pat. No. 4,692,497 discloses a golf ball and material thereof formed by curing a diene polymer including polybutadiene and a metal salt of an alpha, beta ethylenically unsaturated acid using at least two free radical initiators.

U.S. Pat. No. 4,931,376 discloses a process for producing butadiene polymers for use in various applications, including golf ball cover materials. One embodiment of the invention employs a blended polymeric resin material, including at least 30 percent by weight of a trans-polybutadiene polymer as a golf ball cover on a two-piece ball. In a preferred embodiment, the golf ball cover material contains a blend including 30 to 90 percent by weight of a trans-polybutadiene polymer.

U.S. Pat. No. 4,971,329 discloses a solid golf ball made from a polybutadiene admixture of cis-1,4 polybutadiene and 1,2 polybutadiene, a metal salt of an unsaturated carboxylic acid, an inorganic filler, and a free radical initiator.

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The admixture has about 99.5 percent to about 95 percent by weight of cis-1,4 polybutadiene and about 0.5 percent to about 5 percent by weight of 1,2 polybutadiene.

U.S. Pat. No. 5,252,652 discloses a one-piece or multi-layered golf ball core with improved flying performance from a rubber composition comprising a base rubber, preferably 1,4-polybutadiene with a cis-content of at least 40 mole percent, an unsaturated carboxylic acid metal salt, an organic peroxide, and an organic sulfur compound and/or a metal salt thereof. The organic sulfur compound and/or a metal salt is typically present in an amount from about 0.05 to 2 parts per hundred by weight and the organic peroxide is typically present in an amount from about 0.5 to 3 parts per hundred by weight of the total polymer component.

European Patent No. 0 577 058 discloses a golf ball containing a core and a cover that is formed as two separate layers. The inner layer of the cover is molded over the core and is formed from ionomer resin. The outer layer of the cover is molded over the inner layer and is formed from a blend of natural or synthetic balata and a crosslinkable elastomer, such as polybutadiene. In one embodiment of the outer layer of the cover, the elastomer is 1,4-polybutadiene having a cis-structure of at least 40 percent, with the remaining 60 percent being the trans-isomer. A preferred embodiment contains a cis-structure of at least 90 percent and more preferably, a cis-structure of at least 95 percent.

U.S. Pat. No. 5,421,580 discloses a wound golf ball having a liquid center contained in a center bag, a rubber thread layer formed on the liquid center, and a cover over the wound layer and liquid center. The cover material can include any one of a number of materials, or blends thereof, known to those of ordinary skill in the art, including trans-polybutadiene and/or 1,2-polybutadiene (vinyl), such that the cover has a JIS-C hardness of 70-85; preferred trans-percentages are not disclosed.

U.S. Pat. No. 5,697,856 discloses a solid golf ball having a core and a cover wherein the core is produced by vulcanizing a base rubber composition containing a butadiene rubber having a cis-polybutadiene structure content of not less than 90 percent before vulcanization. The amount of trans-polybutadiene structure present after vulcanization is 10 to 30 percent, as amounts over 30 percent are alleged to detrimentally result in cores that are too soft with deteriorated resilience performance, and to cause a decrease in golf ball performance. The core includes a vulcanizing agent, a filler, an organic peroxide, and an organosulfur compound.

British Patent No. 2,321,021 discloses a solid golf ball having a core and a cover formed on the core and having a two-layered cover construction having an inner cover layer and an outer cover layer. The outer cover layer is comprised of a rubber composite that contains 0.05 to 5 parts by weight of an organic sulfide compound. The core rubber composition comprises a base rubber, preferably 1,4-polybutadiene having a cis-content of at least 40 percent by weight, a crosslinking agent, a co-crosslinking agent, an organic sulfide, and a filler. The crosslinking agent is typically an organic peroxide present in an amount from 0.3 to 5.0 parts by weight and the co-crosslinking agent is typically a metal salt of an unsaturated fatty acid present in an amount from 10 to 40 parts by weight. The organic sulfide compound is typically present from 0.05 to 5 parts by weight.

U.S. Pat. No. 5,816,944 discloses a solid golf ball having a core and a cover wherein the core has a JIS-C hardness of 50 to 80 and the cover has a Shore-D hardness of 50 to 60. The core material includes vulcanized rubber, such as cis-polybutadiene, with a crosslinker, an organic peroxide, an

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organosulfur compound and/or a metal-containing organosulfur compound, and a filler.

Additionally, conventional polymers that have a high percentage of the trans-polybutadiene conformation, such as DIENE 35NF, from Firestone Corp., that has 40 percent cis-isomer and 50 percent trans-polybutadiene isomer, and mixtures of high-cis- and high-trans-polybutadiene isomers, such as CARIFLEX BR1220, from Shell Corporation, and FUREN 88, from Asahi Chemical Co., respectively, typically do not yield high resilience values and therefore are not desirable.

In addition to changing center or core ingredients to affect golf ball performance characteristics, a number of patents have issued that are directed towards modifying the properties of layers and covers used in forming a variety of golf balls, such as wound balls, conventional solid balls, multi-layer balls having dual cover layers, dual core layers, and/or balls having a mantle layer disposed between the cover and the core. The most common polymers used by manufacturers in golf ball layers and covers have been ionomers, such as SURLYN, commercially available from E. I. DuPont de Nemours and Co., of Wilmington, Del. Recently, however, manufacturers have investigated the use of alternative polymers, such as polyurethane. For example, U.S. Pat. No. 3,147,324 is directed to a method of making a golf ball having a polyurethane cover.

Polyurethanes have been recognized as useful materials for golf ball covers since about 1960. Polyurethane is the product of a reaction between a polyurethane prepolymer and a curing agent. The polyurethane prepolymer is a product formed by a reaction between a polyol and a diisocyanate. The curing agents used previously are typically diamines or glycols. A catalyst is often employed to promote the reaction between the curing agent and the polyurethane prepolymer.

Since 1960, various companies have investigated the usefulness of polyurethane as a golf ball cover material. U.S. Pat. No. 4,123,061 teaches a golf ball made from a polyurethane prepolymer of polyether and a curing agent, such as a trifunctional polyol, a tetrafunctional polyol, or a diamine. U.S. Pat. No. 5,334,673 discloses the use of two categories of polyurethane available on the market, i.e., thermoset and thermoplastic polyurethanes, for forming golf ball covers and, in particular, thermoset polyurethane covered golf balls made from a composition of polyurethane prepolymer and a slow-reacting amine curing agent, and/or a difunctional glycol. The first commercially successful polyurethane covered golf ball was the Titleist® Professional ball, first released in 1993.

Unlike SURLYN® or ionomer-covered golf balls, polyurethane golf ball covers can be formulated to possess the soft "feel" of balata covered golf balls. However, golf ball covers made from polyurethane have not, to date, fully matched SURLYN®-covered golf balls with respect to resilience or the rebound that is a function of the initial velocity of a golf ball after impact with a golf club.

U.S. Pat. No. 3,989,568 discloses a three-component system employing either one or two polyurethane prepolymers and one or two polyols or fast-reacting diamine curing agents. The reactants chosen for the system must have different rates of reactions within two or more competing reactions.

U.S. Pat. No. 4,123,061 discloses a golf ball made from a polyurethane prepolymer of polyether and a curing agent, such as a trifunctional polyol, a tetrafunctional polyol, or a fast-reacting diamine curing agent.

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U.S. Pat. No. 5,334,673 discloses a golf ball cover made from a composition of a polyurethane prepolymer and a slow-reacting polyamine curing agent and/or a difunctional glycol. Resultant golf balls are found to have improved shear resistance and cut resistance compared to covers made from balata or SURLYN®.

U.S. Pat. No. 5,692,974 discloses methods of using cationic ionomers in golf ball cover compositions. Additionally, the patent relates to golf balls having covers and cores incorporating urethane ionomers. Improved resiliency and initial velocity are achieved by the addition of an alkylating agent such as *t*-butyl-chloride which induces ionic interactions in the polyurethane to produce cationic type ionomers.

International Patent Application WO 98/37929 discloses a composition for golf ball covers that comprises a blend of a diisocyanate/polyol prepolymer and a curing agent comprising a blend of a slow-reacting diamine and a fast-reacting diamine. Improved "feel", playability, and durability characteristics are exhibited.

Conventional polyurethane elastomers are known to have lower resiliency than SURLYN® and other ionomer resins. It has now been discovered that the use of a polyurethane composition, according to the present invention, in forming golf ball cores, intermediate and mantle layers, and/or covers, can raise the velocity of a golf ball prepared with the composition: (1) closer to the velocities observed with SURLYN®-covered golf balls; and (2) higher than the velocities exhibited using alternative urethane compositions. Additionally, it is desired to combine polyurethane cover compositions with polybutadiene core materials, especially those having resilience indices greater than about 40. Cores formed of materials such as these have been found to provide exceptional resiliency characteristics without a loss in performance characteristics (i.e., decreased compression).

It is thus desired to prepare golf balls having lower compression, i.e., a softer ball, while having the same or higher resilience than conventional balls. It is alternatively desired to obtain the same or lower compression while achieving greater resilience.

## SUMMARY OF THE INVENTION

The present invention is directed to a golf ball comprising a center comprising a polybutadiene having a molecular weight of greater than 200,000 and a resilience index of at least about 40; and a cover layer comprising a polyurethane composition formed from a prepolymer having no greater than 7.5 percent by weight unreacted isocyanate groups. Preferably, the resilience index is greater than about 50.

The prepolymer may include an isocyanate, at least one polyol, and at least one curing agent. Preferably, the isocyanate includes 4,4'-diphenylmethane diisocyanate, polymeric 4,4'-diphenylmethane diisocyanate, carbodiimide-modified liquid 4,4'-diphenylmethane diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, *p*-phenylene diisocyanate, toluene diisocyanate, isophoronediiisocyanate, *p*-methylxylene diisocyanate, *m*-methylxylene diisocyanate, *o*-methylxylene diisocyanate, or a mixture thereof. The at least one polyol may include polyether polyols, hydroxy-terminated polybutadiene, polyester polyols, polycaprolactone polyols, polycarbonate polyols, and mixtures thereof. The curing agent may include a polyamine curing agent, a polyol curing agent, or a mixture thereof. It is preferred, however, that the curing agent is a polyamine curing agent.

If the polyamine is selected as the curing agent, the polyamine curing agent may include 3,5-dimethylthio-2,4-toluenediamine and isomers thereof; 3,5-diethylthio-2,4-

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diamine and isomers thereof; 4,4'-bis-(*sec*-butylamino)-diphenylmethane; 1,4-bis-(*sec*-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); trimethylene glycol-di-*p*-aminobenzoate; polytetramethyleneoxide-di-*p*-aminobenzoate; *N,N'*-dialkyldiamino diphenyl methane; *p*, *p'*-methylene dianiline; phenylenediamine; 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(2,6-diethylaniline); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenylmethane; 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); and mixtures thereof.

In one embodiment, however, the curing agent is a polyol curing agent. If the curing agent is a polyol, preferably, the polyol curing agent includes ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy) benzene; 1,3-bis-(2-(2-hydroxyethoxy)ethoxy)benzene; 1,3-bis-(2-[2-(2-hydroxyethoxy)ethoxy]ethoxy)benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-hydroxyethyl ether; hydroquinone-di-( $\beta$ -hydroxyethyl) ether; trimethylol propane, and mixtures thereof.

In another embodiment, the prepolymer has between about 2.5 percent and about 7.5 percent by weight unreacted isocyanate groups. The cover layer preferably has a thickness of less than about 0.05 inches. Further, the center should have a Mooney viscosity of between about 40 and about 80 and, preferably, between about 45 and about 60. In a preferred embodiment, the polybutadiene has a vinyl-polybutadiene isomer content of less than about 2 percent by weight and the polybutadiene has a *cis*-isomer content of at least about 95 percent by weight.

The golf ball center outer diameter is preferably of no less than about 1.55 inches and, additionally, the center further includes a material formed from a conversion reaction of polybutadiene having a first amount of *trans*-polybutadiene, a free radical source, and at least one *cis*-to-*trans* catalyst. Preferably, the reaction occurs at a temperature sufficient to form a polybutadiene reaction product having an second amount of *trans*-polybutadiene greater than the first amount of *trans*-polybutadiene. The *cis*-to-*trans* catalyst may include at least one of a organosulfur component, an inorganic sulfur compound, an aromatic organometallic compound, a metal-organosulfur compound, tellurium, selenium, elemental sulfur, a polymeric sulfur, or an aromatic organic compound. The organosulfur component may include at least one of 4,4'-diphenyl disulfide, 4,4'-ditolyl disulfide, or 2,2'-benzamido diphenyl disulfide. Preferably, the *cis*-to-*trans* catalyst is present in an amount from about 0.1 to 10 parts per hundred of polybutadiene.

In another embodiment, the golf ball further includes an intermediate layer juxtaposed between the center and the cover layer, wherein the intermediate layer comprises a material formed from a conversion reaction of polybutadiene having a first amount of *trans*-polybutadiene, a free radical source, and a *cis*-to-*trans* catalyst comprising at least one organosulfur component, wherein the intermediate layer has an outer diameter of no less than about 1.58 inches, and wherein the center has an outer diameter of less than about 1.55 inches. In yet another embodiment, the cover layer comprises an inner cover layer and an outer cover layer, the inner cover layer juxtaposed the center and the outer cover layer. Preferably, at least one of the inner and outer cover layer has a thickness of less than about 0.05 inches.

If present, the inner cover layer is formed from at least one material selected from the group comprising of an ionomer

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resin, a polyurethane, a polyetherester, a polyetheramide, a polyester, a dynamically vulcanized elastomer, a functionalized styrenebutadiene elastomer, a metallocene polymer, nylon, acrylonitrile butadiene-styrene copolymer or blends thereof. In still another embodiment, the inner cover has an outer diameter of at least about 1.55 inches and, preferably, between about 1.58 and about 1.64 inches. In an additional embodiment, the polyurethane is a thermoplastic or thermoset material.

The present invention is also directed to a golf ball comprising a center comprising a polybutadiene having a molecular weight of greater than 300,000 and a resilience index of at least about 40; an outer core layer having an outer diameter of no less than about 1.51 inches; an inner cover layer surrounding the outer core layer; and an outer cover layer comprising of a polyurethane composition formed from a prepolymer having no greater than about 7.5 percent by weight unreacted isocyanate groups. Preferably, the resilience index is greater than about 50.

The prepolymer may include an isocyanate, at least one polyol, and at least one curing agent. Preferably, the isocyanate includes 4,4'-diphenylmethane diisocyanate, polymeric 4,4'-diphenylmethane diisocyanate, carbodiimide-modified liquid 4,4'-diphenylmethane diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, p-phenylene diisocyanate, toluene diisocyanate, isophoronediiisocyanate, p-methylxylene diisocyanate, m-methylxylene diisocyanate, o-methylxylene diisocyanate, or a mixture thereof. The at least one polyol may include polyether polyols, hydroxy-terminated polybutadiene, polyester polyols, polycaprolactone polyols, polycarbonate polyols, and mixtures thereof. The curing agent may include a polyamine curing agent, a polyol curing agent, or a mixture thereof. It is preferred, however, that the curing agent is a polyamine curing agent.

If the polyamine is selected as the curing agent, the polyamine curing agent may include 3,5-dimethylthio-2,4-toluenediamine and isomers thereof; 3,5-diethylthio-2,4-diamine and isomers thereof; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); trimethylene glycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkyldiamino diphenyl methane; p,p'-methylene diamine; phenylenediamine; 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(2,6-diethylaniline); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenylmethane; 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); and mixtures thereof.

In one embodiment, however, the curing agent is a polyol curing agent. If the curing agent is a polyol, preferably, the polyol curing agent includes ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy) benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy] benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy] ethoxy benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di(-hydroxyethyl) ether; hydroquinone-di(-hydroxyethyl) ether; trimethylol propane, and mixtures thereof.

In a another embodiment, the prepolymer has between about 2.5 percent and about 7.5 percent by weight unreacted isocyanate groups. At least one of the inner and outer cover layers preferably has a thickness of less than about 0.05 inches. Further, the center should have a Mooney viscosity of between about 40 and about 80. In a preferred

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embodiment, the polybutadiene has a vinyl-polybutadiene isomer content of less than about 2 percent by weight and the polybutadiene has a cis-isomer content of at least about 95 percent by weight.

The golf ball center outer diameter is preferably of no less than about 1.55 inches and, additionally, the center further includes a material formed from a conversion reaction of polybutadiene having a first amount of trans-polybutadiene, a free radical source, and at least one cis-to-trans catalyst. Preferably, the reaction occurs at a temperature sufficient to form a polybutadiene reaction product having a second amount of trans-polybutadiene greater than the first amount of trans-polybutadiene. The cis-to-trans catalyst may include at least one of an organosulfur compound, an inorganic sulfur compound, an aromatic organometallic compound, a metal-organosulfur compound, tellurium, selenium, elemental sulfur, a polymeric sulfur, or an aromatic organic compound. The organosulfur component may include at least one of 4,4'-diphenyl disulfide, 4,4'-ditolyl disulfide, or 2,2'-benzamido diphenyl disulfide. Preferably, the cis-to-trans catalyst is present in an amount from about 0.1 to 10 parts per hundred of polybutadiene.

In one embodiment, the inner cover layer includes an ionomer resin, a polyurethane, a polyetherester, a polyetheramide, a polyester, a dynamically vulcanized elastomer, a functionalized styrenebutadiene elastomer, a metallocene polymer nylon, acrylonitrile butadiene-styrene copolymer or blends thereof. The inner cover may have an outer diameter of at least about 1.55 inches and, preferably, between about 1.58 and about 1.64 inches. In an additional embodiment, the polyurethane is a thermoplastic or thermoset material.

The present invention is also directed to a golf ball comprising a center formed of a cis-polybutadiene having a molecular weight of greater than 300,000 and a resilience index of at least about 40; an outer core layer having an outer diameter of no less than about 1.51 inches; an inner cover layer surrounding the outer core layer, the inner cover layer comprising a polyurethane; and an outer cover layer comprising an ionomer or an elastomeric material.

The present invention is also directed to a golf ball comprising a center comprising a polybutadiene having a molecular weight of greater than 300,000 and a resilience index of at least about 40; an outer core layer having an outer diameter of no less than about 1.51 inches; an inner cover layer surrounding the outer core layer; and an outer cover layer; wherein the inner and outer cover layers are formed of a polyurethane composition.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a two-piece golf ball having a cover and a core according to the invention;

FIG. 2 is a cross-section of a golf ball having an intermediate layer between a cover and a center according to the invention; and

FIG. 3 is a cross-section of a golf ball having more than one intermediate layer between a cover and a center according to the invention.

#### DEFINITIONS

The term "about," as used herein in connection with one or more numbers or numerical ranges, should be understood to refer to all such numbers, including all numbers in a range.

As used herein, "cis-to-trans catalyst" means any component or a combination thereof that will convert at least a

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portion of cis-polybutadiene isomer to trans-polybutadiene isomer at a given temperature. It should be understood that the combination of the cis-isomer, the trans-isomer, and any vinyl-isomer, measured at any given time, comprises 100 percent of the polybutadiene.

As used herein, the term "active ingredients" is defined as the specific components of a mixture or blend that are essential to the chemical reaction.

As used herein, substituted and unsubstituted "aryl" groups means a hydrocarbon ring bearing a system of conjugated double bonds, typically comprising  $4n+2\pi$  ring electrons, where  $n$  is an integer. Examples of aryl groups include, but are not limited to phenyl, naphthyl, anisyl, tolyl, xylenyl and the like. According to the present invention, aryl also includes heteroaryl groups, e.g., pyrimidine or thiophene. These aryl groups may also be substituted with any number of a variety of functional groups. In addition to the functional groups described herein in connection with carbocyclic groups, functional groups on the aryl groups can include hydroxy and metal salts thereof; mercapto and metal salts thereof; halogen; amino, nitro, cyano, and amido; carboxyl including esters, acids, and metal salts thereof; silyl; acrylates and metal salts thereof; sulfonyl or sulfonamide; and phosphates and phosphites; and a combination thereof.

As used herein, the term "Atti compression" is defined as the deflection of an object or material relative to the deflection of a calibrated spring, as measured with an Atti Compression Gauge, that is commercially available from Atti Engineering Corp. of Union City, N.J. Atti compression is typically used to measure the compression of a golf ball. When the Atti Gauge is used to measure cores having a diameter of less than 1.680 inches, it should be understood that a metallic or other suitable shim is used to make the measured object 1.680 inches in diameter. However, when referring to the compression of a core, it is preferred to use a compressive load measurement. The term "compressive load" is defined as the normalized load in pounds for a 10.8-percent diametrical deflection for a spherical object having a diameter of 1.58 inches.

As used herein, substituted and unsubstituted "carbocyclic" means cyclic carbon-containing compounds, including, but not limited to cyclopentyl, cyclohexyl, cycloheptyl, adamantyl, and the like. Such cyclic groups may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Such functional groups include those described above, and lower alkyl groups having from 1-28 carbon atoms. The cyclic groups of the invention may further comprise a heteroatom.

As used herein, the term "coefficient of restitution" for golf balls is defined as the ratio of the rebound velocity to the inbound velocity when balls are fired into a rigid plate. The inbound velocity is understood to be 125 ft/s.

As used herein, the term "dynamic stiffness" is defined as load divided by the deflection for a 1.4-mm spherical radius penetration probe oscillating at 1 Hz with an amplitude of 100  $\mu$ m. The probe dynamically penetrates the surface of a sample material. Material samples of spherical cores were prepared by sectioning out a 6-mm-thick layer along the equator of core to produce a disk 6 mm thick with one surface containing the geometric center of the core. By positioning the probe at any selected radial position on the disk, a dynamic stiffness measurement may be obtained. Accurate dynamic measurements may be made by keeping the material sample at a substantially uniform temperature. The dynamic stiffness was acquired using a Dynamic

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Mechanical Analyzer, Model DMA 2980 available from TA Instruments Corporation of New Castle, Del. The instrument setting for the DMA 2980 were 1-Hz frequency, 100- $\mu$ m amplitude, 0.3-N static load, and auto strain of 105 percent. The 1.4-mm spherical radius probe is available from TA Instruments as a penetration kit accessory to the DMA 2980. The DMA 2980 is equipped with a temperature-controlled chamber that enables testing at a wide variety of ambient temperatures.

The method and instrument utilized for measuring "dynamic stiffness" may also be used to measure loss tangent (also commonly referred to as  $\tan \delta$ ). Loss tangent is the ratio of loss modulus to storage modulus. Loss modulus is the portion of modulus which is out of phase with displacement and storage modulus is the portion of modulus which is in phase with displacement. The DMA 2980 automatically calculates and reports loss tangent.

As used herein, the terms "Group VIA component" or "Group VIA element" mean a component that includes a sulfur component, a selenium component, or a tellurium component, or a combination thereof.

As used herein, the term "sulfur component" means a component that is elemental sulfur, polymeric sulfur, or a combination thereof. It should be further understood that "elemental sulfur" refers to the ring structure of  $S_8$  and that "polymeric sulfur" is a structure including at least one additional sulfur relative to the elemental sulfur.

As used herein, the term "fluid" includes a liquid, a paste, a gel, a gas, or any combination thereof.

As used herein, the term "molecular weight" is defined as the absolute weight average molecular weight. The molecular weight is determined by the following method: approximately 20 mg of polymer is dissolved in 10 mL of tetrahydrofuran ("THF"), which may take a few days at room temperature depending on the polymer's molecular weight and distribution. One liter of THF is filtered and degassed before being placed in a high-performance liquid chromatography ("HPLC") reservoir. The flow rate of the HPLC is set to 1 mL/min through a Viscotek column. This non-shedding, mixed bed, column model GMH<sub>HR</sub>-H, which has an ID of 7.8 mm and 300 mm long is available from Viscotek Corp. of Houston, Tex. The THF flow rate is set to 1 mL/min for at least one hour before sample analysis is begun or until stable detector baselines are achieved. During this purging of the column and detector, the internal temperature of the Viscotek TDA Model 300 triple detector should be set to 40° C. This detector is also available from Viscotek Corp. The three detectors (i.e., Refractive Index, Differential Pressure, and Light Scattering) and the column should be brought to thermal equilibrium, and the detectors should be purged and zeroed, to prepare the system for calibration according to the instructions provided with this equipment. A 100- $\mu$ L aliquot of sample solution can then be injected into the equipment and the molecular weight of each sample can be calculated with the Viscotek's triple detector software. When the molecular weight of the polybutadiene material is measured, a dn/dc of 0.130 should always be used. It should be understood that this equipment and these methods provide the molecular weight numbers described and claimed herein, and that other equipment or methods will not necessarily provide equivalent values as used herein.

As used herein, the term "multilayer" means at least two layers and includes liquid center balls, wound balls, hollow-center balls, and balls with at least two intermediate layers and/or an inner or outer cover.

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As used herein, the term "parts per hundred," also known as "phr," is defined as the number of parts by weight of a particular component present in a mixture, relative to 100 parts by weight of the total polymer component. Mathematically, this can be expressed as the weight of an ingredient divided by the total weight of the polymer, multiplied by a factor of 100.

As used herein, the term "substantially free" means less than about 5 weight percent, preferably less than about 3 weight percent, more preferably less than about 1 weight percent, and most preferably less than about 0.01 weight percent.

As used herein the term "resilience index" is defined as the difference in loss tangent measured at 10 cpm and 1000 cpm divided by 990 (the frequency span) multiplied by 100,000 (for normalization and unit convenience). The loss tangent is measured using an RPA 2000 manufactured by Alpha Technologies of Akron, Ohio. The RPA 2000 is set to sweep from 2.5 to 1000 cpm at a temperature of 100° C. using an arc of 0.5 degrees. An average of six loss tangent measurements were acquired at each frequency and the average is used in calculation of the resilience index. The computation of resilience index is as follows:

$$\text{Resilience Index} = 100,000 \{ (\text{loss tangent@10 cpm}) - (\text{loss tangent@1000 cpm}) \} / 990$$

#### DETAILED DESCRIPTION OF THE INVENTION

Referring to FIG. 1, a golf ball 10 of the present invention can include a core 12, a cover 16, and optional inner cover layer 16a surrounding the core 12. Referring to FIG. 2, a golf ball 20 of the present invention can include a center 22, a cover 26, an inner cover layer 26a, and at least one intermediate layer 24 disposed between the cover and the center. Each of the cover and center may also include more than one layer; i.e., the golf ball can be a conventional three-piece wound ball, a two-piece ball, a ball having a multi-layer core or an intermediate layer or layers, etc. Thus, referring to FIG. 3, a golf ball 30 of the present invention can include a center 32, a cover 38, and intermediate layers 34 and 36 disposed between the cover and the center. Although FIG. 3 shows only two intermediate layers, it will be appreciated that any number or type of intermediate layers may be used, as desired.

The present invention relates to two piece golf balls having a core and a cover, or multilayer golf balls having a solid, hollow, or fluid-filled center, a cover, and at least one intermediate layer disposed concentrically adjacent to the center. At least one of the center or optional intermediate layer includes a reaction product that includes a cis-to-trans catalyst, a resilient polymer component having polybutadiene, a free radical source, and optionally, a crosslinking agent, a filler, or both. Preferably, the reaction product has a first dynamic stiffness measured at -50° C. that is less than about 130 percent of a second dynamic stiffness measured at 0° C. More preferably, the first dynamic stiffness is less than about 125 percent of the second dynamic stiffness. Most preferably, the first dynamic stiffness is less than about 110 percent of the second dynamic stiffness.

The invention also includes a method to convert the cis-isomer of the polybutadiene resilient polymer component to the trans-isomer during a molding cycle and to form a golf ball. Various combinations of polymers, cis-to-trans catalysts, fillers, crosslinkers, and a source of free radicals, may be used. To obtain a higher resilience and lower

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compression center or intermediate layer, a high-molecular weight polybutadiene with a cis-isomer content preferably greater than about 90 percent is converted to increase the percentage of trans-isomer content at any point in the golf ball or portion thereof, preferably to increase the percentage throughout substantially all of the golf ball or portion thereof, during the molding cycle. More preferably, the cis-polybutadiene isomer is present in an amount of greater than about 95 percent of the total polybutadiene content. Without wishing to be bound by any particular theory, it is believed that a low amount of 1,2-polybutadiene isomer ("vinyl-polybutadiene") is desired in the initial polybutadiene, and the reaction product. Typically, the vinyl polybutadiene isomer content is less than about 7 percent. Preferably, the vinyl polybutadiene isomer content is less than about 4 percent. More preferably, the vinyl polybutadiene isomer content is less than about 2 percent. Without wishing to be bound by any particular theory, it is also believed that the resulting mobility of the combined cis- and trans-polybutadiene backbone is responsible for the lower modulus and higher resilience of the reaction product and golf balls including the same.

To produce a polymer reaction product that exhibits the higher resilience and lower modulus (low compression) properties that are desirable and beneficial to golf ball playing characteristics, high-molecular-weight cis-1,4-polybutadiene, preferably may be converted to the trans-isomer during the molding cycle. The polybutadiene material typically has a molecular weight of greater than about 200,000. Preferably, the polybutadiene molecular weight is greater than about 250,000, more preferably between about 300,000 and 500,000. Without wishing to be bound by any particular theory, it is believed that the cis-to-trans catalyst component, in conjunction with the free radical source, acts to convert a percentage of the polybutadiene polymer component from the cis- to the trans-conformation. The cis-to-trans conversion requires the presence of a cis-to-trans catalyst, such as an organosulfur or metal-containing organosulfur compound, a substituted or unsubstituted aromatic organic compound that does not contain sulfur or metal, an inorganic sulfide compound, an aromatic organometallic compound, or mixtures thereof. The cis-to-trans catalyst component may include one or more of the other cis-to-trans catalysts described herein.

In one embodiment, the at least one organosulfur component is substantially free of metal, which typically means less than about 10 weight percent metal, preferably less than about 3 weight percent metal, more preferably less than about 1 weight percent metal, and most preferably only trace amounts of metal, such as less than about 0.01 weight percent.

As used herein when referring to the invention, the term "organosulfur compound(s)" or "organosulfur component(s)," means at least one of 4,4'-diphenyl disulfide; 4,4'-ditolyl disulfide; 2,2'-benzamido diphenyl disulfide; bis(2-aminophenyl)disulfide; bis(4-aminophenyl)disulfide; bis(3-aminophenyl)disulfide; 2,2'-bis(4-aminonaphthyl)disulfide; 2,2'-bis(3-aminonaphthyl)disulfide; 2,2'-bis(4-aminonaphthyl)disulfide; 2,2'-bis(5-aminonaphthyl)disulfide; 2,2'-bis(6-aminonaphthyl)disulfide; 2,2'-bis(7-aminonaphthyl)disulfide; 2,2'-bis(8-aminonaphthyl)disulfide; 1,1'-bis(2-aminonaphthyl)disulfide; 1,1'-bis(3-aminonaphthyl)disulfide; 1,1'-bis(4-aminonaphthyl)disulfide; 1,1'-bis(5-aminonaphthyl)disulfide; 1,1'-bis(6-aminonaphthyl)disulfide; 1,1'-bis(7-aminonaphthyl)disulfide; 1,1'-bis(8-aminonaphthyl)disulfide; 1,2'-diamino-1,2'-

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dithiodinaphthalene; 2,3'-diamino-1,2'-dithiodinaphthalene; bis(4-chlorophenyl)disulfide; bis(2-chlorophenyl)disulfide; bis(3-chlorophenyl)disulfide; bis(4-bromophenyl)disulfide; bis(2-bromophenyl)disulfide; bis(3-bromophenyl)disulfide; bis(4-fluorophenyl)disulfide; bis(4-iodophenyl)disulfide; bis(2,5-dichlorophenyl)disulfide; bis(3,5-dichlorophenyl)disulfide; bis(2,4-dichlorophenyl)disulfide; bis(2,6-dichlorophenyl)disulfide; bis(2,5-dibromophenyl)disulfide; bis(3,5-dibromophenyl)disulfide; bis(2-chloro-5-bromophenyl)disulfide; bis(2,4,6-trichlorophenyl)disulfide; bis(2,3,4,5,6-pentachlorophenyl)disulfide; bis(4-cyanophenyl)disulfide; bis(2-cyanophenyl)disulfide; bis(4-nitrophenyl)disulfide; bis(2-nitrophenyl)disulfide; 2,2'-dithiobenzoic acid ethylester; 2,2'-dithiobenzoic acid methylester; 2,2'-dithiobenzoic acid; 4,4'-dithiobenzoic acid ethylester; bis(4-acetylphenyl)disulfide; bis(2-acetylphenyl)disulfide; bis(4-formylphenyl)disulfide; bis(4-carbamoylphenyl)disulfide; 1,1'-dinaphthyl disulfide; 2,2'-dinaphthyl disulfide; 1,2'-dinaphthyl disulfide; 2,2'-bis(1-chlorodinaphthyl)disulfide; 2,2'-bis(1-bromodinaphthyl)disulfide; 1,1'-bis(2-chloronaphthyl)disulfide; 2,2'-bis(1-cyanonaphthyl)disulfide; 2,2'-bis(1-acetylnaphthyl)disulfide; and the like; or a mixture thereof. Preferred organosulfur components include 4,4'-diphenyl disulfide, 4,4'-ditolyl disulfide, or 2,2'-benzamido diphenyl disulfide, or a mixture thereof. A more preferred organosulfur component includes 4,4'-ditolyl disulfide. The organosulfur cis-to-trans catalyst, when present, is preferably present in an amount sufficient to produce the reaction product so as to contain at least about 12 percent trans-polybutadiene isomer, but typically is greater than about 32 percent trans-polybutadiene isomer based on the total resilient polymer component. Suitable metal-containing organosulfur components include, but are not limited to, cadmium, copper, lead, and tellurium analogs of diethyldithiocarbamate, diamyldithiocarbamate; and dimethyldithiocarbamate, or mixtures thereof. Suitable substituted or unsubstituted aromatic organic components that do not include sulfur or a metal include, but are not limited to, 4,4'-diphenyl acetylene, azobenzene, or a mixture thereof. The aromatic organic group preferably ranges in size from  $C_6$  to  $C_{20}$ , and more preferably from  $C_6$  to  $C_{10}$ . Suitable inorganic sulfide components include, but are not limited to titanium sulfide, manganese sulfide, and sulfide analogs of iron, calcium, cobalt, molybdenum, tungsten, copper, selenium, yttrium, zinc, tin, and bismuth. The cis-to-trans catalyst may also be a blend of an organosulfur component and an inorganic sulfide component.

A substituted or unsubstituted aromatic organic compound may also be included in the cis-to-trans catalyst. In one embodiment, the aromatic organic compound is substantially free of metal. Suitable substituted or unsubstituted aromatic organic components include, but are not limited to, components having the formula  $(R_1)_x-R_3-M-R_4-(R_2)_y$ , wherein  $R_1$  and  $R_2$  are each hydrogen or a substituted or unsubstituted  $C_{1-20}$  linear, branched, or cyclic alkyl, alkoxy, or alkylthio group, or a single, multiple, or fused ring  $C_6$  to  $C_{24}$  aromatic group;  $x$  and  $y$  are each an integer from 0 to 5;  $R_3$  and  $R_4$  are each selected from a single, multiple, or fused ring  $C_6$  to  $C_{24}$  aromatic group; and  $M$  includes an azo group or a metal component.  $R_3$  and  $R_4$  are each preferably selected from a  $C_6$  to  $C_{10}$  aromatic group, more preferably selected from phenyl, benzyl, naphthyl, benzamido, and benzothiazyl.  $R_1$  and  $R_2$  are each preferably selected from a substituted or unsubstituted  $C_{1-10}$  linear, branched, or cyclic alkyl, alkoxy, or alkylthio group or a  $C_6$  to  $C_{10}$  aromatic group. When  $R_1$ ,  $R_2$ ,  $R_3$ , or  $R_4$  are substituted, the substitution may include one or more of the following substituent

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groups: hydroxy and metal salts thereof; mercapto and metal salts thereof; halogen; amino, nitro, cyano, and amido; carboxyl including esters, acids, and metal salts thereof; silyl; acrylates and metal salts thereof; sulfonyl or sulfonamide; and phosphates and phosphites. When  $M$  is a metal component, it may be any suitable elemental metal available to those of ordinary skill in the art. Typically, the metal will be a transition metal, although preferably it is tellurium or selenium.

The cis-to-trans catalyst can also include a Group VIA component, as defined herein. Elemental sulfur and polymeric sulfur are commercially available from, e.g., Elastochem, Inc. of Chardon, Ohio. Exemplary sulfur catalyst compounds include PB(RM-S)-80 elemental sulfur and PB(CRST)-65 polymeric sulfur, each of which is available from Elastochem, Inc. An exemplary tellurium catalyst under the tradename TELLOY and an exemplary selenium catalyst under the tradename VANDEX are each commercially available from RT Vanderbilt.

The cis-to-trans catalyst is preferably present in an amount from about 0.1 to 10 parts per hundred of the total resilient polymer component. More preferably, the cis-to-trans catalyst is present in an amount from about 0.1 to 5 parts per hundred of the total resilient polymer component. Most preferably, the cis-to-trans catalyst is present in an amount from about 0.1 to 8 parts per hundred of the total resilient polymer component. The cis-to-trans catalyst is typically present in an amount sufficient to produce the reaction product so as to increase the trans-polybutadiene isomer content to contain from about 5 percent to 70 percent trans-polybutadiene based on the total resilient polymer component.

The measurement of trans-isomer content of polybutadiene referred to herein was and can be accomplished as follows. Calibration standards are prepared using at least two polybutadiene rubber samples of known trans-content, e.g., high and low percent trans-polybutadiene. These samples are used alone and blended together in such a way as to create a ladder of trans-polybutadiene content of at least about 1.5% to 50% or to bracket the unknown amount, such that the resulting calibration curve contains at least about 13 equally spaced points.

Using a commercially available Fourier Transform Infrared ("FTIR") spectrometer equipped with a Photoacoustic ("PAS") cell, a PAS spectrum of each standard was obtained using the following instrument parameters: scan at speed of 2.5 KHz (0.16 cm/s optical velocity), use a 1.2 KHz electronic filter, set an undersampling ratio of 2 (number of laser signal zero crossings before collecting a sample), co-add a minimum of 128 scans at a resolution of  $4\text{ cm}^{-1}$  over a range of 375 to  $4000\text{ cm}^{-1}$  with a sensitivity setting of 1.

The cis-, trans-, and vinyl-polybutadiene peaks are typically found between 600 and  $1100\text{ cm}^{-1}$  in the PAS spectrum. The area under each of the trans-polybutadiene peaks can be integrated. Determining the fraction of each peak area relative to the total area of the three isomer peaks allow construction of a calibration curve of the trans-polybutadiene area fraction versus the actual trans-polybutadiene content. The correlation coefficient ( $R^2$ ) of the resulting calibration curve must be a minimum of 0.95.

A PAS spectrum is obtained, using the parameters described above, for the unknown core material at the point of interest (e.g., the surface or center of the core) by filling the PAS cell with a sample containing a freshly cut, uncontaminated surface free of foreign matters, such as mold release and the like. The trans-polybutadiene area fraction of

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the unknown is analyzed to determine the actual trans-isomer content from the calibration curve.

In one known circumstance when barium sulfate is included, the above method for testing trans-content may be less accurate. Thus, an additional or alternative test of the trans-content of polybutadiene is as follows. Calibration standards are prepared using at least two polybutadienes of known trans-content (e.g., high and low percent trans-polybutadiene). These samples are used alone and blended together in such a way as to create a ladder of trans-polybutadiene content of at least about 1.5% to 50% or to bracket the unknown amount, such that the resulting calibration curve contains at least about 13 equally spaced points.

Using a Fourier Transform Raman ("FT-Raman") spectrometer equipped with a near-infrared laser, a Stokes Raman spectrum should be obtained from each standard using the following instrument parameters: sufficient laser power to obtain a good signal-to-noise ratio ("S/N") without causing excessive heating or fluorescence (typically about 400 to 800 mW is suitable); a resolution of  $2\text{ cm}^{-1}$ ; over a Raman shift spectral range of about 400 to  $4000\text{ cm}^{-1}$ ; and co-adding at least 300 scans.

A calibration curve may be constructed from the data generated above, using a chemometrics approach and software such as PLSplus/IQ from Galactic Industries Corp. of Salem, NE. An acceptable calibration was obtained with this software using a PLS-1 curve generated using an SNV (detrend) pathlength correction, a mean center data preparation, and a 5-point SG second derivative over the spectral range from about 1600 to  $1700\text{ cm}^{-1}$ . The correlation coefficient ( $R^2$ ) of the resulting calibration curve must be a minimum of 0.95.

A Raman spectrum of the core material is obtained using this instrument at the point of interest in the sample (e.g., surface or center of the golf ball core). The sample must be free of foreign matter, such as mold release, etc. Analyze the spectrum of the sample using the PLS calibration curve to determine trans-polybutadiene isomer content of the sample.

A free-radical source, often alternatively referred to as a free-radical initiator, is required in the composition and method. The free-radical source is typically a peroxide, and preferably an organic peroxide. Suitable free-radical sources include di-t-amyl peroxide, di(2-t-butylperoxyisopropyl) benzene peroxide, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, dicumyl peroxide, di-t-butyl peroxide, 2,5-di(t-butylperoxy)-2,5-dimethyl hexane, n-butyl-4,4-bis(t-butylperoxy)valerate, lauryl peroxide, benzoyl peroxide, t-butyl hydroperoxide, and the like, and any mixture thereof. The peroxide is typically present in an amount greater than about 0.1 parts per hundred of the total resilient polymer component, preferably about 0.1 to 15 parts per hundred of the resilient polymer component, and more preferably about 0.2 to 5 parts per hundred of the total resilient polymer component. It should be understood by those of ordinary skill in the art that the presence of certain cis-to-trans catalysts according to the invention may require a larger amount of free-radical source, such as the amounts described herein, compared to conventional cross-linking reactions. The free radical source may alternatively or additionally be one or more of an electron beam, UV or gamma radiation, x-rays, or any other high energy radiation source capable of generating free radicals. It should be further understood that heat often facilitates initiation of the generation of free radicals.

Crosslinkers are included to increase the hardness of the reaction product. Suitable crosslinking agents include one or

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more metallic salts of unsaturated fatty acids or monocarboxylic acids, such as zinc, calcium, or magnesium acrylate salts, and the like, and mixtures thereof. Preferred acrylates include zinc acrylate, zinc diacrylate, zinc methacrylate, and zinc dimethacrylate, and mixtures thereof. The crosslinking agent must be present in an amount sufficient to crosslink a portion of the chains of polymers in the resilient polymer component. For example, the desired compression may be obtained by adjusting the amount of crosslinking. This may be achieved, for example, by altering the type and amount of crosslinking agent, a method well-known to those of ordinary skill in the art. The crosslinking agent is typically present in an amount greater than about 0.1 percent of the resilient polymer component, preferably from about 10 to 40 percent of the resilient polymer component, more preferably from about 10 to 30 percent of the resilient polymer component. When an organosulfur is selected as the cis-to-trans catalyst, zinc diacrylate may be selected as the crosslinking agent and is present in an amount of less than about 25 phr.

Fillers added to one or more portions of the golf ball typically include processing aids or compounds to affect rheological and mixing properties, the specific gravity (i.e., density-modifying fillers), the modulus, the tear strength, reinforcement, and the like. The fillers are generally inorganic, and suitable fillers include numerous metals or metal oxides, such as zinc oxide and tin oxide, as well as barium sulfate, zinc sulfate, calcium carbonate, barium carbonate, clay, tungsten, tungsten carbide, an array of silicas, and mixtures thereof. Fillers may also include various foaming agents or blowing agents which may be readily selected by one of ordinary skill in the art. Polymeric, ceramic, metal, and glass microspheres may be solid or hollow, and filled or unfilled. Fillers are typically also added to one or more portions of the golf ball to modify the density thereof to conform to uniform golf ball standards. Fillers may also be used to modify the weight of the center or at least one additional layer for specialty balls, e.g., a lower weight ball is preferred for a player having a low swing speed.

The polymers, free-radical initiator, filler(s), and any other materials used in forming either the golf ball center or any portion of the core, in accordance with invention, may be combined to form a mixture by any type of mixing known to one of ordinary skill in the art. Suitable types of mixing include single pass and multi-pass mixing, and the like. The crosslinking agent, and any other optional additives used to modify the characteristics of the golf ball center or additional layer(s), may similarly be combined by any type of mixing. A single-pass mixing process where ingredients are added sequentially is preferred, as this type of mixing tends to increase efficiency and reduce costs for the process. The preferred mixing cycle is single step wherein the polymer, cis-trans catalyst, filler, zinc diacrylate, and peroxide are added sequentially. Suitable mixing equipment is well known to those of ordinary skill in the art, and such equipment may include a Banbury mixer, a two-roll mill, or a twin screw extruder. Conventional mixing speeds for combining polymers are typically used, although the speed must be high enough to impart substantially uniform dispersion of the constituents. On the other hand, the speed should not be too high, as high mixing speeds tend to break down the polymers being mixed and particularly may undesirably decrease the molecular weight of the resilient polymer component. The speed should thus be low enough to avoid high shear, which may result in loss of desirably high molecular weight portions of the polymer component. Also, too high a mixing speed may undesirably result in creation

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of enough heat to initiate the crosslinking before the preforms are shaped and assembled around a core. The mixing temperature depends upon the type of polymer components, and more importantly, on the type of free-radical initiator. For example, when using di(2-t-butyl-peroxyisopropyl) benzene as the free-radical initiator, a mixing temperature of about 80° C. to 125° C., preferably about 88° C. to 110° C., and more preferably about 90° C. to 100° C. is suitable to safely mix the ingredients. Additionally, it is important to maintain a mixing temperature below the peroxide decomposition temperature. For example, if dicumyl peroxide is selected as the peroxide, the temperature should not exceed 200° F. Suitable mixing speeds and temperatures are well-known to those of ordinary skill in the art, or may be readily determined without undue experimentation.

The mixture can be subjected to, e.g., a compression or injection molding process, to obtain solid spheres for the center or hemispherical shells for forming an intermediate layer. The polymer mixture is subjected to a molding cycle in which heat and pressure are applied while the mixture is confined within a mold. The cavity shape depends on the portion of the golf ball being formed. The compression and heat liberates free radicals by decomposing one or more peroxides, which may initiate the cis-to-trans conversion and crosslinking simultaneously. The temperature and duration of the molding cycle are selected based upon the type of peroxide and cis-trans catalyst selected. The molding cycle may have a single step of molding the mixture at a single temperature for a fixed time duration. An example of a single step molding cycle, for a mixture that contains dicumyl peroxide, would hold the polymer mixture at 340° F. for a duration of 15 minutes. The molding cycle may also include a two-step process, in which the polymer mixture is held in the mold at an initial temperature for an initial duration of time, followed by holding at a second, typically higher temperature for a second duration of time. An example of a two-step molding cycle would be holding the mold at 290° F. for 40 minutes, then ramping the mold to 340° F. where it is held for a duration of 20 minutes. In a preferred embodiment of the current invention, a single-step cure cycle is employed. Single-step processes are effective and efficient, reducing the time and cost of a two-step process. The resilient polymer component, polybutadiene, cis-to-trans conversion catalyst, additional polymers, free-radical initiator, filler, and any other materials used in forming either the golf ball center or any portion of the core, in accordance with the invention, may be combined to form a golf ball by an injection molding process, which is also well-known to one of ordinary skill in the art. Although the curing time depends on the various materials selected, a particularly suitable curing time is about 5 to 18 minutes, preferably from about 8 to 15 minutes, and more preferably from about 10 to 12 minutes. Those of ordinary skill in the art will be readily able to adjust the curing time upward or downward based on the particular materials used and the discussion herein.

The cured resilient polymer component, which contains a greater amount of trans-polybutadiene than the uncured resilient polymer component, is formed into an article having a first hardness at a point in the interior and a surface having a second hardness such that the second hardness differs from the first hardness by greater than 10 percent of the first hardness. Preferably, the article is a sphere and the point is the midpoint of the article. In another embodiment, the second hardness differs from the first by greater than 20 percent of the first hardness. The cured article also has a first amount of trans-polybutadiene at an interior location and a

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second amount of trans-polybutadiene at a surface location, wherein the first amount is at least about 6 percent less than the second amount, preferably at least about 10 percent less than the second amount, and more preferably at least about 20 percent less than the second amount. The interior location is preferably a midpoint and the article is preferably a sphere. The compression of the core, or portion of the core, of golf balls prepared according to the invention is preferably below about 50, more preferably below about 25.

The cover provides the interface between the ball and a club. Properties that are desirable for the cover are good moldability, high abrasion resistance, high tear strength, high resilience, and good mold release, among others. The cover typically has a thickness to provide sufficient strength, good performance characteristics and durability. The cover preferably has a thickness of less than about 0.1 inches, more preferably, less than about 0.05 inches, and most preferably, between about 0.02 and about 0.04 inches. The invention is particularly directed towards a multilayer golf ball which comprises a core, an inner cover layer, and an outer cover layer. In this embodiment, preferably, at least one of the inner and outer cover layers has a thickness of less than about 0.05 inches, more preferably between about 0.02 and about 0.04 inches. Most preferably, the thickness of either layer is about 0.03 inches.

When the golf ball of the present invention includes an intermediate layer, such as an inner cover layer, this layer can include any materials known to those of ordinary skill in the art, including thermoplastic and thermosetting materials, but preferably the intermediate layer can include any suitable materials, such as ionic copolymers of ethylene and an unsaturated monocarboxylic acid which are available under the trademark SURLYN of E. I. DuPont de Nemours & Co., of Wilmington, Del., or IOTEX or ESCOR of Exxon. These are copolymers or terpolymers of ethylene and methacrylic acid or acrylic acid partially neutralized with salts of zinc, sodium, lithium, magnesium, potassium, calcium, manganese, nickel or the like, in which the salts are the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially neutralized and might include methacrylic, crotonic, maleic, fumaric or itaconic acid.

This golf ball can likewise include one or more homopolymeric or copolymeric intermediate materials, such as:

- (1) Vinyl resins, such as those formed by the polymerization of vinyl chloride, or by the copolymerization of vinyl chloride with vinyl acetate, acrylic esters or vinylidene chloride;
- (2) Polyolefins, such as polyethylene, polypropylene, polybutylene and copolymers such as ethylene methylacrylate, ethylene ethylacrylate, ethylene vinyl acetate, ethylene methacrylic or ethylene acrylic acid or propylene acrylic acid and copolymers and homopolymers produced using a single-site catalyst or a metallocene catalyst;
- (3) Polyurethanes, such as those prepared from polyols and diisocyanates or polyisocyanates and those disclosed in U.S. Pat. No. 5,334,673;
- (4) Polyureas, such as those disclosed in U.S. Pat. No. 5,484,870;
- (5) Polyamides, such as poly(hexamethylene adipamide) and others prepared from diamines and dibasic acids, as well as those from amino acids such as poly(caprolactam), and blends of polyamides with

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SURLYN, polyethylene, ethylene copolymers, ethyl-propylene-non-conjugated diene terpolymer, and the like;

- (6) Acrylic resins and blends of these resins with poly vinyl chloride, elastomers, and the like;
- (7) Thermoplastics, such as urethanes; olefinic thermoplastic rubbers, such as blends of polyolefins with ethylene-propylene-non-conjugated diene terpolymer; block copolymers of styrene and butadiene, isoprene or ethylene-butylene rubber; or copoly(ether-amide), such as PEBAX, sold by ELF Atochem of Philadelphia, Pa.;
- (8) Polyphenylene oxide resins or blends of polyphenylene oxide with high impact polystyrene as sold under the trademark NORYL by General Electric Company of Pittsfield, Mass.;
- (9) Thermoplastic polyesters, such as polyethylene terephthalate, polybutylene terephthalate, polyethylene terephthalate/glycol modified and elastomers sold under the trademarks HYTREL by E. I. DuPont de Nemours & Co. of Wilmington, Del., and LOMOD by General Electric Company of Pittsfield, Mass.;
- (10) Blends and alloys, including polycarbonate with acrylonitrile butadiene styrene, polybutylene terephthalate, polyethylene terephthalate, styrene maleic anhydride, polyethylene, elastomers, and the like, and polyvinyl chloride with acrylonitrile butadiene styrene or ethylene vinyl acetate or other elastomers; and
- (11) Blends of thermoplastic rubbers with polyethylene, propylene, polyacetal, nylon, polyesters, cellulose esters, and the like.

Preferably, the optional intermediate layer includes polymers, such as ethylene, propylene, butene-1 or hexane-1 based homopolymers or copolymers including functional monomers, such as acrylic and methacrylic acid and fully or partially neutralized ionomer resins and their blends, methyl acrylate, methyl methacrylate homopolymers and copolymers, imidized, amino group containing polymers, polycarbonate, reinforced polyamides, polyphenylene oxide, high impact polystyrene, polyether ketone, polysulfone, poly(phenylene sulfide), acrylonitrile-butadiene, acrylic-styrene-acrylonitrile, poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene vinyl alcohol), poly(tetrafluoroethylene) and their copolymers including functional comonomers, and blends thereof. Suitable cover compositions also include a polyether or polyester thermoplastic urethane, a thermoset polyurethane, a low modulus ionomer, such as acid-containing ethylene copolymer ionomers, including E/X/Y terpolymers where E is ethylene, X is an acrylate or methacrylate-based softening comonomer present in about 0 to 50 weight percent and Y is acrylic or methacrylic acid present in about 5 to 35 weight percent. More preferably, in a low spin rate embodiment designed for maximum distance, the acrylic or methacrylic acid is present in about 15 to 35 weight percent, making the ionomer a high modulus ionomer. In a high spin embodiment, the cover includes an ionomer where an acid is present in about 10 to 15 weight percent and includes a softening comonomer.

The cover preferably include a polyurethane composition comprising the reaction product of at least one polyisocyanate, polyol, and at least one curing agent.

Any polyisocyanate available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyisocyanates include, but are not limited to, 4,4'-diphenylmethane diisocyanate ("MDI"), polymeric MDI,

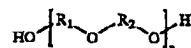
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carbodiimide-modified liquid MDI, 4,4'-dicyclohexylmethane diisocyanate ("HH<sub>12</sub>MDI"), p-phenylene diisocyanate ("PPDI"), toluene diisocyanate ("TDI"), 3,3'-dimethyl-4,4'-biphenylene diisocyanate ("TODI"), isophoronediiisocyanate ("IPDI"), hexamethylene diisocyanate ("HDI"), naphthalene diisocyanate ("NDI"), xylene diisocyanate ("XDI"); para-tetramethylxylene diisocyanate ("p-TMXDI"); meta-tetramethylxylene diisocyanate ("m-TMXDI"); ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; cyclohexyl diisocyanate; 1,6-hexamethylene-diisocyanate ("HDI"); dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-

isocyanatomethylcyclohexane; methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,4,4-trimethyl-1,6-hexane diisocyanate ("TMDI"), tetracene diisocyanate, naphthalene diisocyanate, anthracene diisocyanate, and mixtures thereof. Polyisocyanates are known to those of ordinary skill in the art as having more than one isocyanate group, e.g., di-, tri-, and tetra-isocyanate. Preferably, the polyisocyanate includes MDI, PPDI, TDI, or a mixture thereof, and more preferably, the polyisocyanate includes MDI. It should be understood that, as used herein, the term "MDI" includes 4,4'-diphenylmethane diisocyanate, polymeric MDI, carbodiimide-modified liquid MDI, and mixtures thereof and, additionally, that the diisocyanate employed may be "low free monomer," understood by one of ordinary skill in the art to have lower levels of "free" monomer isocyanate groups, typically less than about 0.1% free monomer groups. Examples of "low free monomer" diisocyanates include, but are not limited to Low Free Monomer MDI, Low Free Monomer TDI, and Low Free Monomer PPDI.

The at least one polyisocyanate should have less than about 14% unreacted NCO groups. Preferably, the at least one polyisocyanate has no greater than about 7.5% NCO, more preferably, between about 2.5% and about 7.5%, and most preferably, between about 4% to about 6.5%.

Any polyol available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyols include, but are not limited to, polyether polyols, hydroxy-terminated polybutadiene (including partially/fully hydrogenated derivatives), polyester polyols, polycaprolactone polyols, and polycarbonate polyols. In one preferred embodiment, the polyol includes polyether polyol, more preferably those polyols that have the generic structure:

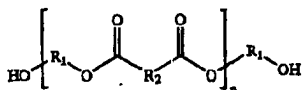


where R<sub>1</sub> and R<sub>2</sub> are straight or branched hydrocarbon chains, each containing from 1 to about 20 carbon atoms, and n ranges from 1 to about 45. Examples include, but are not limited to, polytetramethylene ether glycol ("PTMEG"), polyethylene propylene glycol, polyoxypropylene glycol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds and substituted or unsubstituted aromatic and cyclic groups. Preferably, the polyol of the present invention includes PTMEG.

In another embodiment, polyester polyols are included in the polyurethane material of the invention. Preferred polyester polyols have the generic structure:

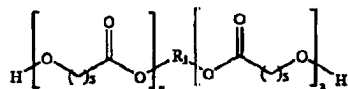
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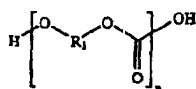
where  $\text{R}_1$  and  $\text{R}_2$  are straight or branched hydrocarbon chains, each containing from 1 to about 20 carbon atoms, and  $n$  ranges from 1 to about 25. Suitable polyester polyols include, but are not limited to, polyethylene adipate glycol, polybutylene adipate glycol, polyethylene propylene adipate glycol, ortho-phthalate-1,6-hexanediol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

In another embodiment, polycaprolactone polyols are included in the materials of the invention. Preferably, any polycaprolactone polyols have the generic structure:



where  $\text{R}_1$  is a straight chain or branched hydrocarbon chain containing from 1 to about 20 carbon atoms, and  $n$  is the chain length and ranges from 1 to about 20. Suitable polycaprolactone polyols include, but are not limited to, 1,6-hexanediol-initiated polycaprolactone, diethylene glycol initiated polycaprolactone, trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

In yet another embodiment, the polycarbonate polyols are included in the polyurethane material of the invention. Preferably, any polycarbonate polyols have the generic structure:



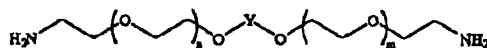
where  $\text{R}_1$  is predominantly bisphenol A units  $-(\text{p-C}_6\text{H}_4)-\text{C}(\text{CH}_3)_2-(\text{p-C}_6\text{H}_4)-$  or derivatives thereof, and  $n$  is the chain length and ranges from 1 to about 20. Suitable polycarbonates include, but are not limited to, polyphthalate carbonate. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups. In one embodiment, the molecular weight of the polyol is from about 200 to about 4000.

Polyamine curatives are also suitable for use in the polyurethane composition of the invention and have been found to improve cut, shear, and impact resistance of the resultant balls. Preferred polyamine curatives include, but are not limited to, 3,5-dimethylthio-2,4-toluenediamine and isomers thereof; 3,5-diethyltoluene-2,4-diamine and isomers thereof, such as 3,5-diethyltoluene-2,6-diamine; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkyldiamino diphenyl methane; p,p'-methylene dianiline ("MDA"); m-phenylenediamine ("MPDA"); 4,4'-

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methylene-bis-(2-chloroaniline) ("MOCA"); 4,4'-methylene-bis-(2,6-diethylaniline); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenylmethane; 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); trimethylene glycol di-p-aminobenzoate; and mixtures thereof. Preferably, the curing agent of the present invention includes 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, such as ETHACURE 300, commercially available from Albermarle Corporation of Baton Rouge, La. Suitable polyamine curatives, which include both primary and secondary amines, preferably have molecular weights ranging from about 64 to about 2000.

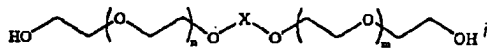
Other suitable polyamine curatives include those having the general formula:



where  $n$  and  $m$  each separately have values of 0, 1, 2, or 3, and where  $\text{Y}$  is 1,2-cyclohexyl, 1,3-cyclohexyl, 1,4-cyclohexyl, ortho-phenylene, meta-phenylene, or para-phenylene, or a combination thereof. Preferably,  $n$  and  $m$ , each separately, have values of 0, 1, or 2, and preferably, 1 or 2.

At least one of a diol, triol, tetraol, or hydroxy-terminated curatives may be added to the aforementioned polyurethane composition. Suitable diol, triol, and tetraol groups include ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis-(2-hydroxyethoxy) benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(β-hydroxyethyl)ether; hydroquinone-di-(β-hydroxyethyl)ether; and mixtures thereof. Preferred hydroxy-terminated curatives include ethylene glycol; diethylene glycol; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol, trimethylol propane, and mixtures thereof.

Preferably, the hydroxy-terminated curatives have molecular weights ranging from about 48 to 2000. It should be understood that molecular weight, as used herein, is the absolute weight average molecular weight and would be understood as such by one of ordinary skill in the art. Other suitable hydroxy-terminated curatives have the following general chemical structure:



where  $n$  and  $m$  each separately have values of 0, 1, 2, or 3, and where  $\text{X}$  is ortho-phenylene, meta-phenylene, para-phenylene, 1,2-cyclohexyl, 1,3-cyclohexyl, or 1,4-cyclohexyl, or mixtures thereof. Preferably,  $n$  and  $m$  each separately have values of 0, 1, or 2, and more preferably, 1 or 2.

Both the hydroxy-terminated and amine curatives can include one or more saturated, unsaturated, aromatic, and cyclic groups. Additionally, the hydroxy-terminated and amine curatives can include one or more halogen groups. The polyurethane composition can be formed with a blend or mixture of curing agents. If desired, however, the polyurethane composition may be formed with a single curing agent.

Any method known to one of ordinary skill in the art may be used to combine the polyisocyanate, polyol, and curing

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agent of the present invention. One commonly employed method, known in the art as a one-shot method, involves concurrent mixing of the polyisocyanate, polyol, and curing agent. This method results in a mixture that is inhomogeneous (more random) and affords the manufacturer less control over the molecular structure of the resultant composition. A preferred method of mixing is known as a prepolymer method. In this method, the polyisocyanate and the polyol are mixed separately prior to addition of the curing agent. This method affords a more homogeneous mixture resulting in a more consistent polymer composition.

An optional filler component may be chosen to impart additional density to blends of the previously described components. The selection of such filler(s) is dependent upon the type of golf ball desired (i.e., one-piece, two-piece multi-component, or wound). Examples of useful fillers include zinc oxide, barium sulfate, calcium oxide, calcium carbonate and silica, as well as the other well known corresponding salts and oxides thereof. Additives, such as nanoparticles, glass spheres, and various metals, such as titanium and tungsten, can be added to the polyurethane compositions of the present invention, in amounts as needed, for their well-known purposes. Additional components which can be added to the polyurethane composition include UV stabilizers and other dyes, as well as optical brighteners and fluorescent pigments and dyes. Such additional ingredients may be added in any amounts that will achieve their desired purpose.

Due to the very thin nature, it has been found by the present invention that the use of a castable, reactive material, which is applied in a fluid form, makes it possible to obtain very thin outer cover layers on golf balls. Specifically, it has been found that castable, reactive liquids, which react to form a urethane elastomer material, provide desirable very thin outer cover layers.

The castable, reactive liquid employed to form the urethane elastomer material can be applied over the inner core using a variety of application techniques such as spraying, dipping, spin coating, or flow coating methods which are well known in the art. An example of a suitable coating technique is that which is disclosed in U.S. Pat. No. 5,733, 428, filed May 2, 1995 entitled "Method And Apparatus For Forming Polyurethane Cover On A Golf Ball", the disclosure of which is hereby incorporated by reference in its entirety in the present application.

The cover is preferably formed around the coated core by mixing and introducing the material in the mold halves. It is important that the viscosity be measured over time, so that the subsequent steps of filling each mold half, introducing the core into one half and closing the mold can be properly timed for accomplishing centering of the core cover halves fusion and achieving overall uniformity. Suitable viscosity range of the curing urethane mix for introducing cores into the mold halves is determined to be approximately between about 2,000 cP and about 30,000 cP, with the preferred range of about 8,000 cP to about 15,000 cP.

To start the cover formation, mixing of the prepolymer and curative is accomplished in motorized mixer including mixing head by feeding through lines metered amounts of curative and prepolymer. Top preheated mold halves are filled and placed in fixture units using pins moving into holes in each mold. After the reacting materials have resided in top mold halves for about 50 to about 80 seconds, a core is lowered at a controlled speed into the gelling reacting mixture. At a later time, a bottom mold half or a series of bottom mold halves have similar mixture amounts introduced into the cavity.

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A ball cup holds the ball core through reduced pressure (or partial vacuum) in hose. Upon location of the coated core in the halves of the mold after gelling for about 50 to about 80 seconds, the vacuum is released allowing core to be released. The mold halves, with core and solidified cover half thereon, are removed from the centering fixture unit, inverted and mated with other mold halves which, at an appropriate time earlier, have had a selected quantity of reacting polyurethane prepolymer and curing agent introduced therein to commence gelling.

Similarly, U.S. Pat. No. 5,006,297 to Brown et al. and U.S. Pat. No. 5,334,673 to Wu both also disclose suitable molding techniques which may be utilized to apply the castable reactive liquids employed in the present invention. The disclosures of these patents are hereby incorporated by reference in their entirety. However, the method of the invention is not limited to the use of these techniques.

Depending on the desired properties, balls prepared according to the invention can exhibit substantially the same or higher resilience, or coefficient of restitution ("COR"), with a decrease in compression or modulus, compared to balls of conventional construction. Additionally, balls prepared according to the invention can also exhibit substantially higher resilience, or COR, without an increase in compression, compared to balls of conventional construction. Another measure of this resilience is the "loss tangent," or  $\tan \delta$ , which is obtained when measuring the dynamic stiffness of an object. Loss tangent and terminology relating to such dynamic properties is typically described according to ASTM D4092-90. Thus, a lower loss tangent indicates a higher resiliency, thereby indicating a higher rebound capacity. Low loss tangent indicates that most of the energy imparted to a golf ball from the club is converted to dynamic energy, i.e., launch velocity and resulting longer distance. The rigidity or compressive stiffness of a golf ball may be measured, for example, by the dynamic stiffness. A higher dynamic stiffness indicates a higher compressive stiffness. To produce golf balls having a desirable compressive stiffness, the dynamic stiffness of the crosslinked reaction product material should be less than about 50,000 N/m at  $-50^{\circ}\text{C}$ . Preferably, the dynamic stiffness should be between about 10,000 and 40,000 N/m at  $-50^{\circ}\text{C}$ , more preferably, the dynamic stiffness should be between about 20,000 and 30,000 N/m at  $-50^{\circ}\text{C}$ .

The dynamic stiffness is similar in some ways to dynamic modulus. Dynamic stiffness is dependent on probe geometry as described herein, whereas dynamic modulus is a unique material property, independent of geometry. The dynamic stiffness measurement has the unique attribute of enabling quantitative measurement of dynamic modulus and exact measurement of loss tangent at discrete points within a sample article. In the case of this invention, the article is a golf ball core. The polybutadiene reaction product preferably has a loss tangent below about 0.1 at  $-50^{\circ}\text{C}$ , and more preferably below about 0.07 at  $-50^{\circ}\text{C}$ .

The resultant golf balls typically have a coefficient of restitution of greater than about 0.7, preferably greater than about 0.75, and more preferably greater than about 0.78. The golf balls also typically have an Atti compression (which has been referred to as PGA compression in the past) of at least about 40, preferably from about 50 to 120, and more preferably from about 60 to 100. The golf ball polybutadiene material of the present invention typically has a flexural modulus of from about 500 psi to 300,000 psi, preferably from about 2000 to 200,000 psi. The golf ball polybutadiene material typically has a hardness of at least about 15 Shore A, preferably between about 30 Shore A and 80 Shore D,

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more preferably between about 50 Shore A and 60 Shore D. The specific gravity is typically greater than about 0.7, preferably greater than about 1, for the golf ball polybutadiene material.

The center composition should comprise at least one rubber material having a resilience index of at least about 40. Preferably the resilience index is at least about 50. A comparison of a number of polybutadiene polymers are listed in Table 1 below. Polymers that produce resilient golf balls and, therefore, are suitable for the present invention, include but are not limited to CB23, CB22, BR60, and 1207G. To clarify the method of computation for resilience index, the resilience index for CB23, for example, is computed as follows:

$$\text{Resilience Index for CB23} = 100,000 \{ (0.954) - (0.407) \} 990 \text{ Resilience Index for CB23} = 55$$

TABLE 1

Resilience Index of example polybutadiene polymers			
Rubber	Tan $\delta$ at		Resilience Index at 100° C.
	10 cps	1000 cps	
CB23	0.954	0.407	55
CB22	0.895	0.358	54
BR-60	0.749	0.350	40
BR-40	0.841	0.446	40
Taklene 8855	0.720	0.414	31
CARIFLEX BR1220	0.487	0.439	5
BUDENE 1207G	0.825	0.388	44

The molding process and composition of golf ball portions typically results in a gradient of material properties. Methods employed in the prior art generally exploit hard-

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Additionally, the unvulcanized rubber, such as polybutadiene, in golf balls prepared according to the invention typically has a Mooney viscosity of between about 40 and about 80, more preferably, between about 45 and about 60, and most preferably, between about 45 and about 55. Mooney viscosity is typically measured according to ASTM D-1646.

When golf balls are prepared according to the invention, they typically will have dimple coverage greater than about 60 percent, preferably greater than about 65 percent, and more preferably greater than about 75 percent. The flexural modulus of the cover on the golf balls, as measured by ASTM method D6272-98, Procedure B, is typically greater than about 500 psi, and is preferably from about 500 psi to 150,000 psi. As discussed herein, the outer cover layer is preferably formed from a relatively soft polyurethane material. In particular, the material of the outer cover layer should have a material hardness, as measured by ASTM-2240, between about 30 and about 60 Shore D, preferably from about 35 to about 55 Shore D. The inner cover layer, if present, preferably has a material hardness from about 50 to about 75 Shore D, preferably from about 60 to about 65 Shore D.

## EXAMPLES

A variety of cores were prepared according to the present invention, as well as some cores prepared using conventional materials. All cores in Table 2 were prepared to a diameter of 1.58 inches. The recipes for each core, and values measured for compression and COR are presented in Table 2 below:

TABLE 2

Golf Ball Core Properties from Various Rubber Formulations						
Ingredients	Mooney viscosity @ 100° C.	1	2	3	4	5
CB23	51	100				
CB22	63		100			
BR-60	60			100		
Taklene 8855	48				100	
CARIFLEX BR1220	43					100
zinc diacrylate peroxide		28	28	28	28	28
zinc oxide		0.53	0.53	0.53	0.53	0.53
tungsten		4.3	4.3	4.3	4.3	4.3
Core Properties		11.0	11.0	11.0	11.0	11.0
compression		77	75	77	76	71
COR @ 125 ft/s		0.815	0.811	0.810	0.807	0.802

ness to quantify these gradients. Hardness is a qualitative measure of static modulus and does not represent the modulus of the material at the deformation rates associated with golf ball use, i.e., impact by a club. As is well known to one skilled in the art of polymer science, the time-temperature superposition principle may be used to emulate alternative deformation rates. For golf ball portions including polybutadiene, a 1-Hz oscillation at temperatures between 0° C. and -50° C. are believed to be qualitatively equivalent to golf ball impact rates. Therefore, measurement of loss tangent and dynamic stiffness at 0° C. to -50° C. may be used to accurately anticipate golf ball performance, preferably at temperatures between about -20° C. and -50° C.

A variety of metal sulfide cis-to-trans catalysts that successfully converted a portion of the cis-polybutadiene isomer to the trans-isomer are presented in Table 3. CARIFLEX BR1220 polybutadiene (100 phr) was reacted with zinc oxide (5 phr), dicumyl peroxide (3 phr), the free radical initiator, and zinc diacrylate (25 phr), to form the reaction product as described in the present invention.

Trans-isomer conversion percentages range from below 8 percent to above 17 percent for the various catalysts that are present in amounts ranging from below 1.7 phr to above 3.7 phr. The table clearly demonstrates the effectiveness of numerous different cis-to-trans catalysts, at varying concentrations, for increasing the trans-polybutadiene content.

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## Example 1

A Core Prepared from According to the Invention,  
Employing an Organosulfur Cis-to-trans Catalyst

A core according to the present invention was created employing an organosulfur compound as the cis-to-trans conversion catalyst. The resultant core properties clearly demonstrate the advantages of a golf ball core made according to the current invention as compared to example cores constructed with conventional technology. The components and physical characteristics are presented in Table 4.

The compressive load of cores prepared according to the invention is approximately half of the compressive load of cores constructed in accordance with U.S. Pat. Nos. 5,697, 856, 5,252,652, and 4,692,497, while at the same time retaining roughly the same, and in some cases higher, COR (resilience). The core made according to the current invention has a lower compressive load (soft), yet is resilient (fast). The compressive load is greater than that of a core constructed in accordance with U.S. Pat. No. 3,239,228, but has a significantly higher COR. The core of U.S. Pat. No. 3,239,228 is very soft and very slow (very low COR).

The percent change in dynamic stiffness from 0° C. to -50° C. was also measured at both the edge and center of the cores. The dynamic stiffness at both the edge and the center

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of the core of the current invention varied only slightly, less than 20 percent, over the temperature range investigated. The core made according to U.S. Pat. No. 3,239,228 varied over 230 percent, whereas the cores made according to other conventional technology, had a dynamic stiffness that varied by greater than 130 percent, and typically by as much as 150 percent, over the same temperature range.

The percent of trans-conversion was also measured at both the center and edge of the core prepared according to the current invention, and for cores prepared as disclosed in the same four patents mentioned above, allowing a trans-gradient to be calculated. The core according to the current invention had a trans-gradient of about 32 percent from edge to center. For the core prepared according to the current invention, the pre- and post-cure trans-percentages was also measured to determine the effectiveness of that process. The percentage of polybutadiene converted to the trans-isomer ranged from almost 40 percent at the center to greater than 55 percent at the edge. Two of the cores prepared according to conventional technology, U.S. Pat. Nos. 3,239,228 and 4,692,497, had a zero trans-gradient. A third core, prepared according to U.S. Pat. No. 5,697,856, had only a slight trans-gradient, less than 18 percent from edge to center. A fourth core, prepared according to U.S. Pat. No. 5,252,652, had a very large gradient, almost 65 percent from edge to center.

TABLE 3

Metal Sulfide Conversion Examples													
CARIFLEX BR1220	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5
Dicumyl peroxide	3	3	3	3	3	3	3	3	3	3	3	3	3
Zinc Diacrylate	25	25	25	25	25	25	25	25	25	25	25	25	25
Cis-to-Trans "Catalyst"													
PoS	2.87												
MnS		2.65											
TiS <sub>2</sub>			1.70										
CaS				2.20									
CoS					2.77								
MoS <sub>2</sub>						2.43							
WS <sub>2</sub>							3.77						
Cu <sub>2</sub> S								4.65					
SeS <sub>2</sub>									2.19				
Y <sub>2</sub> S <sub>3</sub>										2.76			
ZnS											2.97		
Sb <sub>2</sub> S <sub>3</sub>												3.45	
Bi <sub>2</sub> S <sub>3</sub>													5.22
% Trans BR isomer	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Pre-cure													
% Trans BR isomer	10.5	16.1	17.0	8.3	10.3	10.1	9.2	5.8	5.2	10.2	10.1	10.7	10.5
Post-cure													

TABLE 4

Chemical Constituents	Examples of Conventional Golf Balls						
	Examples of Golf Balls of the Invention						
	#1	#2	#3	US #3239228	US #5816944	US #5252652	US #4971329
Polybutadiene (Shell, CARIFLEX BR1220)	100	100	100		N/A	N/A	N/A
Polybutadiene (Firestone, 35 NF)				100	N/A	N/A	N/A
DMDS				2.1	N/A	N/A	N/A
Carbon Black (RA)				15	N/A	N/A	N/A
Wood Flour				24	N/A	N/A	N/A
Sulfur				24	N/A	N/A	N/A
Stearic Acid				1.5	N/A	N/A	N/A
Recores				15	N/A	N/A	N/A

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TABLE 4-continued

Chemical Constituents	Examples of Golf Balls of the Invention				Examples of Conventional Golf Balls		
	#1	#2	#3	US #3239228	US #5816944	US #5252652	US #4692497
Vanox MBPC				2	N/A	N/A	N/A
Trichloroamine				4	N/A	N/A	N/A
Zinc oxide	5	5	5	5	N/A	N/A	N/A
Dicumyl peroxide	3	1.9	2		N/A	N/A	N/A
Zinc Diacrylate	25	25	25		N/A	N/A	N/A
Cis-Trans "Catalyst"					N/A	N/A	N/A
MnS		0.82			N/A	N/A	N/A
Dibutylidinitride	2.5		1.5		N/A	N/A	N/A
Cu <sub>2</sub> S			1		N/A	N/A	N/A
Resultant Core Properties							
Load(lbs) @10.8% Deflection 1.580" core	165.5	191.4	191.8	61.1	325	390	480
Coefficient of Restitution @125 ft/s	0.783	0.777	0.785	0.599	0.779	0.805	0.775
Hardness Shore C							
Surface	61	76	62	35	75	80	80.5
Center	52	52	59	30	70	61	66.5
Dynamic Stiffness @ 0° C. (N/m)							
Edge*	25338	27676	28493	8312	62757	83032	72235
Center	20783	17390	27579	8361	61071	26264	50612
Dynamic Stiffness @ -50° C. (N/m)							
Edge*	30265	34523	34455	19394	92763	109053	108242
Center	23022	20603	32195	18617	89677	28808	83183
Dynamic Stiffness Ratio at -50° C./0° C.							
Edge*	119%	125%	121%	233%	148%	131%	150%
Center	111%	118%	117%	223%	147%	110%	164%
Loss Tangent 0° C.							
Edge*	0.024	0.027	0.024	0.074	0.039	0.037	0.045
Center	0.025	0.023	0.023	0.073	0.033	0.025	0.043
Loss Tangent -50° C.							
Edge*	0.098	0.084	0.097	0.183	0.142	0.119	0.099
Center	0.067	0.071	0.085	0.180	0.129	0.059	0.095
% Trans BR isomer Precure	1.5	1.5	1.5	50	N/A	N/A	N/A
% Trans BR isomer Postcure							
Surface	55.8	8.4	45.5	50	30.2	24.6	1.5
Center	37.8	4.6	25.5	50	24.7	8.5	1.5
% Trans Variation (Surf.-Center)/Surf.	32%	45%	44%	0%	18%	65%	0%

\*Edge is measured approximately 5 mm from the exterior surface of the measured article.

## Example 2

A Core Prepared from According to the Invention,  
Employing an Inorganic Sulfide Cis-to-trans  
Catalyst

A core according to the present invention was created employing an inorganic sulfide compound as the cis-to-trans conversion catalyst. The resultant core properties clearly demonstrate the advantages of a golf ball core made according to the current invention as compared to example cores constructed with conventional technology. The components and physical characteristics are presented in Table 4.

The compressive load is approximately half of the compressive load of three cores constructed in accordance with U.S. Pat. Nos. 5,697,856, 5,252,652, and 4,692,497, while at the same time retaining roughly the same, and in some cases, a higher COR (resilience). The core made according to the current invention is soft, yet resilient (fast). The compressive load is greater than a core constructed in accordance with U.S. Pat. No. 3,239,228, but has a significantly higher COR. The core of U.S. Pat. No. 3,239,228 is very soft and very slow (low COR).

The percent change in dynamic stiffness from 0° C. to -50° C. was also measured at both the edge and center of the cores. The dynamic stiffness at both the edge and the center of the core of the current invention varied only slightly, less than 125 percent, over the temperature range investigated. The core made according to U.S. Pat. No. 3,239,228 varied over 230 percent, whereas the cores made according to other conventional technology, had a dynamic stiffness that varied by greater than 130 percent, and typically by as much as 150 percent, over the same temperature range.

The percent of trans-conversion was also measured at both the center and edge of the core prepared according to the current invention, and for cores prepared according to the same four patents mentioned above, allowing a trans-gradient to be calculated. The core according to the current invention had a trans-gradient of about 45 percent from edge to center. Two of the cores prepared in accordance with U.S. Pat. Nos. 3,239,228 and 4,692,497 had a zero trans-gradient. A third core, prepared in accordance with U.S. Pat. No. 5,697,856, had only a slight trans-gradient, less than 18 percent from edge to center. A fourth core, prepared in accordance with U.S. Pat. No. 5,252,652, had a very large gradient, almost 65 percent, from edge to center.

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## Example 3

A Core Prepared from According to the Invention,  
Employing a Blend of Organosulfur and Inorganic  
Sulfide Cis-to-trans Catalyst

A core according to the present invention was created employing a blend of organosulfur and inorganic sulfide compounds as the cis-to-trans conversion catalyst. The resultant core properties clearly demonstrate the advantages of a golf ball core made according to the current invention as compared to example cores constructed with conventional technology. The components and physical characteristics are presented in Table 4.

The compressive load is approximately half of the compressive load of three cores constructed in accordance with U.S. Pat. Nos. 5,697,856, 5,252,652, and 4,692,497, while at the same time retaining roughly the same, and in some cases a higher COR (resilience). The core made according to the current invention is soft, yet resilient (fast). The compressive load of the invention is greater than a fourth core constructed in accordance with U.S. Pat. No. 3,239,228, but has a significantly higher COR. The core constructed in accordance with U.S. Pat. No. 3,239,228 is very soft and very slow (low COR).

The percent change in dynamic stiffness from 0° C. to -50° C. was also measured at both the edge and center of the cores. The dynamic stiffness at both the edge and the center of the core of the current invention varied only slightly, less than 121 percent, over the temperature range investigated. The core made in accordance with U.S. Pat. No. 3,239,228 varied over 230 percent, whereas the cores made according to other conventional technology had a dynamic stiffness that varied by greater than 130 percent, and typically by as much as 150 percent, over the same temperature range.

The percent of trans-conversion was also measured at both the center and edge of the core prepared according to the current invention, and for cores prepared to the same four patents mentioned above, allowing a trans-gradient to be calculated. The core according to the current invention had a trans-gradient that about 44 percent from edge to center. For the core prepared according to the current invention, the pre- and post-cure trans-percentages was also measured to determine the effectiveness of that process. The percentage of polybutadiene converted to the trans-isomer ranged from almost 26 percent at the center to greater than 45 percent at the edge. Two of the cores prepared in accordance with U.S. Pat. Nos. 3,239,228 and 4,692,497 had a zero trans-gradient. A third core prepared in accordance with U.S. Pat. No. 5,697,856 had only a slight trans-gradient, less than 18 percent from edge to center. A fourth core, prepared in accordance with U.S. Pat. No. 5,252,652 had a very large gradient, almost 65 percent from edge to center.

## Example 4

Comparison of a Conventional Dual Core Ball to  
Dual Core Ball Prepared According to the  
Invention

A dual core golf ball according to the present invention was created having a solid center, an intermediate layer surrounding the solid center, and a multilayer cover disposed concentrically around the intermediate layer. The components and physical characteristics are presented below in Table 5.

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TABLE 5

Center Composition		Example 4: Dual Core	
5	CARIFLEX BR1220	100	
	zinc diacrylate	20	
	dicumyl peroxide	2.5	
	zinc oxide	39	
	DTDS	0.75	
	<u>Center Properties</u>		
10	% trans Precure	1.5	
	% trans Postcure	40	
	load in lbs required (10.8% deflection)	109	
	<u>Mantle Composition</u>		
15	CB23	80	
	zinc diacrylate	38	
	VAROX 231 XL	0.42	
	DBDB-60	0.15	
	zinc oxide	6	
	polyisoprene	20	
20	<u>Inner Cover Composition and Properties</u>		
	Na SURLYN	50	
	Li SURLYN	50	
	Shore D hardness	68	
	thickness	0.03 in	
25	<u>Outer Cover Composition and Properties</u>		
	MDI polyurethane		
	thickness	0.03 in	

A solid center was constructed for the ball of the present invention. The center was created from CARIFLEX BR-1220 polybutadiene as the starting material, the only difference being replacing the VAROX 802-40KE-HP peroxide (conventional technology) with a DTDS cis-to-trans catalyst of the current invention and dicumyl peroxide. This substitution allows a portion of the polybutadiene material to be converted to the trans-configuration during the molding process. The resulting solid center had an outside diameter of approximately 1.15 inches. The polybutadiene reaction product prepared thereby had a trans-isomer content of 40 percent compared to the 1.5 percent trans-isomer of conventional balls. An intermediate layer, having outside diameter of approximately 1.56 inches, was constructed around the solid center to form a core. The outer layer is made of CB23 having a molecular weight of about 360,000 and a Mooney viscosity of about 51.

## Examples 5-8

Comparison of Conventional Golf Balls with Those  
Prepared According to the Invention

A polybutadiene reaction product was prepared for two conventional prior art compositions (Examples 5-6) as well as one prepared according to the invention (Examples 7-8). The recipes for each composition can be seen in Table 6 below.

TABLE 6

Reaction Product	Example 5	Example 6	Example 7	Example 8
	(phr)	(phr)	(phr)	(phr)
60 CARIFLEX BR1220	100	100	100	100
zinc oxide	26.6	2.67	26.6	26.6
65 barium sulfate	—	31	—	—
zinc diacrylate	20	22.3	20	20

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TABLE 6-continued

	Example 5 (phr)	Example 6 (phr)	Example 7 (phr)	Example 8 (phr)
dicumyl peroxide	2	—	2	2
VAROX 802 40KE-HP*	—	0.89	—	—
polymeric sulfur	0	0	0.25	0
elemental sulfur	0	0	0	0.25
pre-cure trans- polybutadiene content	1.5%	1.5%	1.5%	1.5%
Golf Ball Core				
post-cure trans- polybutadiene content in reaction product	1.5%	1.5%	12%	12%
ATI Compression COR	53 n/a <sup>b</sup>	73 0.72	26 0.77	21 0.76

\*A di-(2-*t*-butylisopropylperoxy)-benzene peroxide commercially available from R. T. Vanderbilt of Norwalk, CT.

<sup>b</sup>The core of Example 5 was sufficiently rigid to crack during testing of the coefficient of restitution, indicating an undesirably low COR.

These constituents were mixed and molded, thereby converting a percentage of *cis*- to a *trans*-conformation, in a solid sphere sized like the core of a golf ball. Examples 7-8 illustrate the significant conversion of *cis*-polybutadiene to *trans*-polybutadiene when a sulfur *cis*-to-*trans* catalyst is present according to the invention compared to the lack of conversion in Examples 5-6 when no sulfur catalyst is present. Moreover, Examples 7-8 illustrate the improved coefficient of restitution with no significant change in compression that can be achieved with golf balls including the reaction product according to the invention.

The invention described and claimed herein is not to be limited in scope by the specific embodiments herein disclosed, since these embodiments are intended as illustrations of several aspects of the invention. Any equivalent embodiments are intended to be within the scope of this invention. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

What is claimed is:

1. A golf ball comprising:
  - a center comprising a material formed from the conversion reaction of at least a *cis*-to-*trans* catalyst and a polybutadiene, wherein the material has a molecular weight of greater than about 200,000 and a resilience index of at least about 40;
  - an inner cover layer; and
  - an outer cover layer disposed about the inner cover layer comprising a polyurethane composition.
2. The golf ball of claim 1, wherein the inner cover layer comprises at least one of an ionomer resin, a polyurethane, a polyetherester, a polyetheramide, a polyester, a dynamically vulcanized elastomer, a functionalized styrenebutadiene elastomer, a metallocene polymer nylon, acrylonitrile butadiene-styrene copolymer, or blends thereof.
3. The golf ball of claim 1, wherein the resilience index of the material is at least about 50.
4. The golf ball of claim 1, wherein the *cis*-to-*trans* catalyst comprises at least one of an organosulfur compound, an inorganic sulfur compound, an aromatic organometallic compound, a metal-organosulfur compound, tellurium, selenium, elemental sulfur, a polymeric sulfur, or an aromatic organic compound.
5. The golf ball of claim 1, wherein the polyurethane composition comprises at least one isocyanate, at least one polyol, and at least one curing agent.
6. The golf ball of claim 1, wherein the outer cover layer has a thickness of about 0.02 inches to about 0.04 inches.
7. The golf ball of claim 1, wherein the inner cover layer has an outer diameter of about 1.55 inches or greater.
8. A golf ball comprising:
  - a center formed of a reaction product comprising polybutadiene and a *cis*-to-*trans* catalyst, wherein the reaction product has a molecular weight of greater than about 200,000, and wherein the reaction product comprises greater than about 32 percent *trans*-isomer;
  - an inner cover layer
  - an outer cover layer disposed around the inner cover layer, wherein the outer cover layer comprises a castable reactive liquid material.
9. The golf ball of claim 8, wherein the inner cover layer comprises an ionomer resin, a polyurethane, a polyetherester, a polyetheramide, a polyester, a dynamically vulcanized elastomer, a functionalized styrenebutadiene elastomer, a metallocene polymer nylon, acrylonitrile butadiene-styrene copolymer, or blends thereof.
10. The golf ball of claim 8, wherein the inner cover layer comprises a copolymer of ethylene and an unsaturated monocarboxylic acid, wherein the monocarboxylic acid is at least partially neutralized.
11. The golf ball of claim 10, wherein the monocarboxylic acid is fully neutralized.
12. The golf ball of claim 8, wherein the outer cover layer has a thickness of about 0.02 inches to about 0.04 inches and the inner cover layer has an outer diameter of about 1.55 inches or greater.
13. The golf ball of claim 8, wherein the castable reactive material comprises a prepolymer having less than about 14 percent unreacted isocyanate groups, and wherein the prepolymer is cured with a polyol, polyamine, or a mixture thereof.
14. The golf ball of claim 8, wherein the *cis*-to-*trans* catalyst comprises at least one of an organosulfur compound, an inorganic sulfur compound, an aromatic organometallic compound, a metal-organosulfur compound, tellurium, selenium, elemental sulfur, a polymeric sulfur, or an aromatic organic compound.
15. The golf ball of claim 8, wherein the reaction product has a molecular weight of about 300,000 or greater.
16. A golf ball comprising:
  - a center comprising a material formed from the conversion reaction of at least a *cis*-to-*trans* catalyst and a polybutadiene, wherein the material has a molecular weight of greater than about 200,000 and a resilience index of at least about 40;
  - an inner cover layer; and
  - an outer cover layer disposed about the inner cover layer, comprising a castable reactive liquid material.
17. The golf ball of claim 16, wherein the *cis*-to-*trans* catalyst comprises an organosulfur compound.
18. The golf ball of claim 17, wherein the *cis*-to-*trans* catalyst is present in an amount sufficient to result in the material comprising greater than 32 percent *trans*-polybutadiene isomer.
19. A golf ball of claim 18, wherein the *cis*-to-*trans* catalyst is present in an amount from about 0.1 to 5 parts per hundred based on the total material.
20. The golf ball of claim 16, wherein the resilience index is at least about 50.
21. The golf ball of claim 16, wherein the inner cover layer has a hardness of about 50 to about 75 Shore D.
22. The golf ball of claim 16, wherein the castable reactive liquid material has a material hardness of about 30 Shore D to about 60 Shore D.

\* \* \* \* \*

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# Exhibit 12



US006849006B2

(12) **United States Patent**  
Cavallaro et al.

(10) Patent No.: **US 6,849,006 B2**

(45) Date of Patent: **Feb. 1, 2005**

(54) **THIN, THERMOSET,  
POLYURETHANE-COVERED GOLF BALL  
WITH A DUAL CORE**

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Sep. 13, 2001, now Pat. No. 6,635,716, and a continuation-  
in-part of application No. 09/782,782, filed on Feb. 13,  
2001, which is a continuation of application No. 09/274,015,  
filed on Mar. 22, 1999, which is a continuation of application  
No. 08/863,788, filed on May 27, 1997, now Pat. No.  
5,885,172.

(51) Int. Cl.<sup>7</sup> ..... **A63B 37/04**

(52) U.S. Cl. .... **473/376**

(58) Field of Search ..... **473/376, 377,  
473/373, 374**

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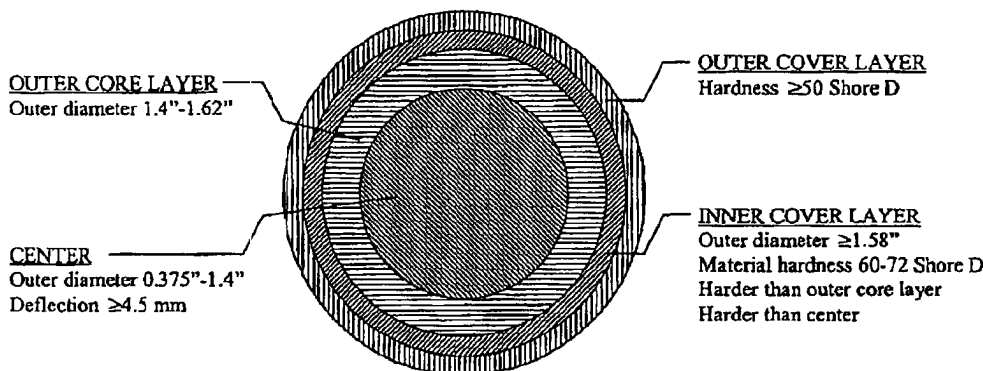
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(57) **ABSTRACT**

A golf ball comprising a core and a cover disposed about the  
core, wherein the core comprises a center and an outer core  
layer, and the cover comprises an inner cover layer and an  
outer cover layer; and wherein the center has an outer  
diameter from about 0.375 inches to about 1.4 inches and  
deflection of greater than about 4.5 mm under a load of 100  
Kg; the outer core layer has an outer diameter of from about  
1.4 in to about 1.62 in; the inner cover layer has an outer  
diameter of greater than about 1.58 in and a material  
hardness of less than about 72 Shore D; and the outer cover  
layer has a hardness of greater than about 50 Shore D and a  
material hardness of less than about 50 Shore D.

**22 Claims, 1 Drawing Sheet**



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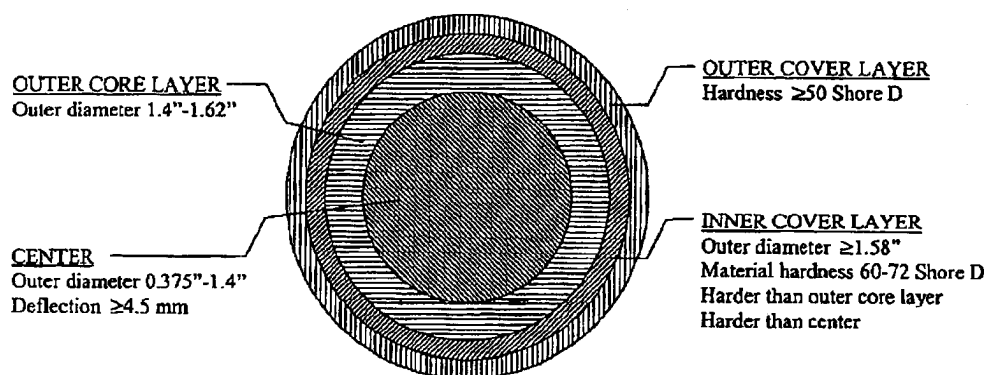
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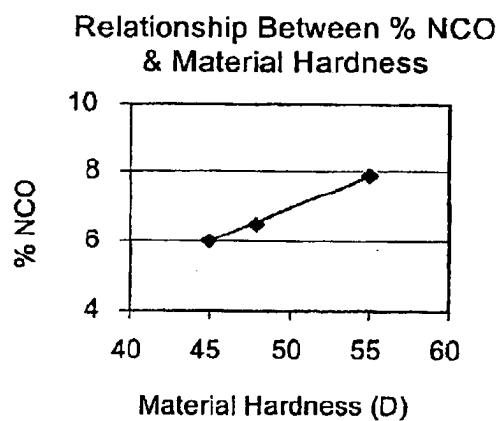
**U.S. Patent**

**Feb. 1, 2005**

**US 6,849,006 B2**



**FIG. 1**



**FIG. 2**

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# THIN, THERMOSET, POLYURETHANE-COVERED GOLF BALL WITH A DUAL CORE

## CROSS REFERENCE TO RELATED APPLICATIONS

This application is 1) a continuation-in-part of application Ser. No. 09/951,963, filed Sep. 13, 2001 now U.S. Pat. No. 6,635,716; as well as 2) a continuation-in-part of application Ser. No. 09/782,782, filed Feb. 13, 2001, which is a continuation-in-part of application Ser. No. 09/274,015, filed Mar. 22, 1999, which is a continuation-in-part of U.S. Pat. No. 5,885,172; file date May 27, 1997 now U.S. Pat. No. 5,885,172.

## FIELD OF THE INVENTION

This invention relates generally to golf balls, and more specifically, to multi-layer golf balls. In particular, this invention relates to a golf ball having a core comprising a center and an outer core layer, and a cover comprising an inner cover layer and an outer cover layer.

## BACKGROUND

Conventional golf balls can be divided into two general classes: solid and wound. Solid golf balls include one-piece, two-piece (i.e., solid core and a cover), and multi-layer (i.e., solid core of one or more layers and/or a cover of one or more layers) golf balls. Wound golf balls typically include a solid, hollow, or fluid-filled center, surrounded by a tensioned elastomeric material, and a cover. Solid balls have traditionally been considered longer and more durable than wound balls, but also lack a particular "feel" provided by the wound construction.

By altering ball construction and composition, manufacturers can vary a wide range of playing characteristics, such as compression, velocity, and spin, each of which can be optimized for various playing abilities. One golf ball component, in particular, that many manufacturers are continually looking to improve is the center or core. The core becomes the "engine" of the golf ball when hit with a club head. Generally, golf ball cores and/or centers are constructed with a polybutadiene-based polymer composition. Compositions of this type are constantly being altered in an effort to provide a higher coefficient of restitution ("COR") while at the same time resulting in a lower compression which, in turn, can lower the golf ball spin rate, provide better "feel," or both. This is a difficult task, however, given the physical limitations of currently-available polymers. As such, there remains a need for novel and improved golf ball core compositions.

It has been determined that, upon addition of a halogenated organosulfur compound or the salts thereof, in particular, pentachlorothiophenol ("PCTP") salt, to polybutadiene rubber compositions, that golf ball cores may be constructed that exhibit increased COR, decreased compression, or both. The present invention is, therefore, directed to golf ball centers and cores that include a halogenated organosulfur compound, or a salt thereof, for embodiments such as these.

## SUMMARY OF THE INVENTION

The present invention is directed to a golf ball comprising a core and a cover disposed about the core, wherein the core comprises a center and an outer core layer, and the cover comprises an inner cover layer and an outer cover layer; and

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wherein the center has an outer diameter from about 0.375 inches to about 1.4 inches and deflection of greater than about 4.5 mm under a load of 100 Kg; the outer core layer has an outer diameter of from about 1.4 in to about 1.62 in; the inner cover layer has an outer diameter of greater than about 1.58 in and a material hardness of less than about 72 Shore D; and the outer cover layer has a hardness of greater than about 50 Shore D and a material hardness of less than about 50 Shore D.

Preferably, the inner cover layer material hardness is between about 60 and about 70 Shore D, and has an outer diameter is from about 1.59 in to about 1.66 inches. The center should have an outer diameter between about 0.5 inches and about 1.25 inches but in a preferred embodiment, the center has an outer diameter no greater than about 1.0 inches. The outer core layer outer has a diameter from about 1.52 inches to about 1.58 inches but in one embodiment, the outer core layer has an outer diameter of at least about 1.55 inches.

In an alternative embodiment, the center has a first hardness, the outer core layer has a second hardness greater than the first, and the inner cover layer has a third hardness greater than the second. Preferably, the outer cover layer has a fourth hardness less than the third hardness.

The center may be solid, liquid, hollow, or air-filled. At least one of the inner or outer cover layers has a thickness of less than about 0.05 inches. The inner cover layer can include an ionomeric material, vinyl resins, polyolefins, polyurethanes, polyureas, polyamides, acrylic resins, thermoplastics, polyphenylene oxide resins, thermoplastic polyesters, thermoplastic rubbers, fully-neutralized polymers, partially-neutralized polymers, and mixtures thereof.

At least one of the center, core layer, or inner and outer cover layers includes polybutadiene rubber composition comprising between about 2.2 parts and about 5 parts of a halogenated organosulfur compound. Suitable halogenated organosulfur compounds include pentafluorothiophenol; 2-fluorothiophenol; 3-fluorothiophenol; 4-fluorothiophenol; 2,3-fluorothiophenol; 2,4-fluorothiophenol; 3,4-fluorothiophenol; 3,5-fluorothiophenol; 2,3,4-fluorothiophenol; 3,4,5-fluorothiophenol; 2,3,4,5-tetrafluorothiophenol; 2,3,5,6-tetrafluorothiophenol; 4-chlorotetrafluorothiophenol; pentachlorothiophenol; 2-chlorothiophenol; 3-chlorothiophenol; 4-chlorothiophenol; 2,3-chlorothiophenol; 2,4-chlorothiophenol; 3,4-chlorothiophenol; 3,5-chlorothiophenol; 2,3,4-chlorothiophenol; 3,4,5-chlorothiophenol; 2,3,4,5-tetrachlorothiophenol; 2,3,5,6-tetrachlorothiophenol; pentabromothiophenol; 2-bromothiophenol; 3-bromothiophenol; 4-bromothiophenol; 2,3-bromothiophenol; 2,4-bromothiophenol; 3,4-bromothiophenol; 3,5-bromothiophenol; 2,3,4-bromothiophenol; 3,4,5-bromothiophenol; 2,3,4,5-tetrabromothiophenol; 2,3,5,6-tetrabromothiophenol; pentaiodothiophenol; 2-iodothiophenol; 3-iodothiophenol; 4-iodothiophenol; 2,3-iodothiophenol; 2,4-iodothiophenol; 3,4-iodothiophenol; 3,5-iodothiophenol; 2,3,4-iodothiophenol; 3,4,5-iodothiophenol; 2,3,4,5-tetraiodothiophenol; 2,3,5,6-tetraiodothiophenol; and their zinc salts, the metal salts thereof, and mixtures thereof.

Preferably, the halogenated organosulfur compound is pentachlorothiophenol or the metal salt thereof, the metal salt is selected from the group consisting of zinc, calcium, magnesium, sodium, and lithium. Most preferably, the metal salt is zinc.

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In one embodiment, the center and the outer core layer are solid and comprise polybutadiene rubber composition comprising between about 2.2 parts and about 5 parts of a halogenated organosulfur compound or the zinc salt thereof. In a preferred embodiment, the center and the outer core layer are solid and the center comprises polybutadiene rubber composition comprising between about 2.2 parts and about 5 parts of a halogenated organosulfur compound or the zinc salt thereof. In an alternative embodiment, the center and the outer core layer are solid and the outer core layer comprises polybutadiene rubber composition comprising between about 2.2 parts and about 5 parts of a halogenated organosulfur compound or the zinc salt thereof.

The core should have an SCDI compression less than about 160. Preferably, the core has an SCDI compression between about 40 and about 160 and most preferably, the core has an SCDI compression between about 60 and about 120.

The polybutadiene composition can further include an  $\alpha,\beta$ -unsaturated carboxylic acid or a metal salt thereof, an organic peroxide, and a filler. The outer cover layer may include a polyurethane composition comprising a prepolymer formed of a polyisocyanate and a polyol, and a curing agent. Preferably, at least one of the prepolymer and curing agent are saturated. In an additional embodiment, the polyurethane composition comprises at least one of a UV absorber, a hindered amine light stabilizer, or an optical brightener.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-section of the golf ball of the present invention; and

FIG. 2 is a graph depicting the relationship between percent isocyanate and material hardness.

#### DETAILED DESCRIPTION

Referring to FIG. 1, the golf ball cores of the present invention may comprise any of a variety of constructions, but preferably include a core formed of a center and at least one outer core layer and a cover formed of an outer cover layer and at least one inner cover layer. The core and/or the cover layers may be formed of more than one layer and an intermediate or mantle layer may be disposed between the core and the cover of the golf ball. The innermost portion of the core, while preferably solid, may be a hollow or a liquid-filled, gel-, or air-filled sphere. As with the core, the cover layers may also comprise a plurality of layers. The core may also comprise a solid or liquid filled center around which many yards of a tensioned elastomeric material are wound.

The materials for solid cores include compositions having a base rubber, a crosslinking agent, a filler, a halogenated organosulfur compound, and a co-crosslinking or initiator agent. The base rubber typically includes natural or synthetic rubbers. A preferred base rubber is 1,4-polybutadiene having a cis-structure of at least 40%, more preferably at least about 90%, and most preferably at least about 95%. Most preferably, the base rubber comprises high-Mooney-viscosity rubber. Preferably, the base rubber has a Mooney viscosity greater than about 35, more preferably greater than about 50. Preferably, the polybutadiene rubber has a molecular weight greater than about 400,000 and a polydispersity of no greater than about 2. Examples of desirable polybutadiene rubbers include BUNA® CB22 and BUNA® CB23, commercially available from Bayer of Akron, Ohio; UBE-POL® 360L and UBE-POL® 150L, commercially available from UBE Industries of Tokyo, Japan; and CARIFLEX®

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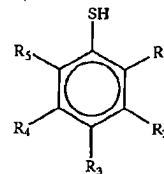
BCP820 and CARIFLEX® BCP824, commercially available from Shell of Houston, Tex. If desired, the polybutadiene can also be mixed with other elastomers known in the art such as natural rubber, polyisoprene rubber and/or styrene-butadiene rubber in order to modify the properties of the core.

The crosslinking agent includes a metal salt, such as a zinc salt or a magnesium unsaturated fatty acid, such as acrylic or methacrylic acid, having 3 to 8 carbon atoms. Examples include, but are not limited to, one or more metal salt diacrylates, dimethacrylates, and monomethacrylates, wherein the metal is magnesium, calcium, zinc, aluminum, sodium, lithium, or nickel. Preferred acrylates include zinc acrylate, zinc diacrylate, zinc methacrylate, zinc dimethacrylate, and mixtures thereof. The crosslinking agent is typically present in an amount greater than about 10 parts per hundred ("pph") parts of the base polymer, preferably from about 20 to 40 pph of the base polymer, more preferably from about 25 to 35 pph of the base polymer.

The initiator agent can be any known polymerization initiator which decomposes during the cure cycle. Suitable initiators include organic peroxide compounds, such as dicumyl peroxide; 1,1-di(t-butylperoxy) 3,3,5-trimethyl cyclohexane;  $\alpha, \alpha$ -bis (t-butylperoxy) diisopropylbenzene; 2,5-dimethyl-2,5 di(t-butylperoxy) hexane; di-t-butyl peroxide; and mixtures thereof. Other examples include, but are not limited to, VAROX® 231XL and VAROX® DCP-R, commercially available from Elf Atochem of Philadelphia, Pa.; PERKODOX® BC and PERKODOX® 14, commercially available from Akzo Nobel of Chicago, Ill. and ELASTOCHEM® DCP-70, commercially available from Rhein Chemie of Trenton, N.J.

It is well known that peroxides are available in a variety of forms having different activity. The activity is typically defined by the "active oxygen content." For example, PERKODOX® BC peroxide is 98% active and has an active oxygen content of 5.80%, whereas PERKODOX® DCP-70 is 70% active and has an active oxygen content of 4.18%. If the peroxide is present in pure form, it is preferably present in an amount of at least about 0.25 pph, more preferably between about 0.35 pph and about 2.5 pph, and most preferably between about 0.5 pph and about 2 pph. Peroxides are also available in concentrate form, which are well-known to have differing activities, as described above. In this case, if concentrate peroxides are employed in the present invention, one skilled in the art would know that the concentrations suitable for pure peroxides are easily adjusted for concentrate peroxides by dividing by the activity. For example, 2 pph of a pure peroxide is equivalent 4 pph of a concentrate peroxide that is 50% active (i.e., 2 divided by 0.5=4).

The halogenated organosulfur compounds of the present invention include, but are not limited to those having the following general formula:



where  $R_1$ - $R_5$  can be  $C_1$ - $C_6$  alkyl groups; halogen groups; thiol groups ( $-SH$ ), carboxylated groups; sulfonated groups; and hydrogen; in any order; and also pentafluoro-

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rothiophenol; 2-fluorothiophenol; 3-fluorothiophenol; 4-fluorothiophenol; 2,3-fluorothiophenol; 2,4-fluorothiophenol; 3,4-fluorothiophenol; 3,5-fluorothiophenol; 2,3,4-fluorothiophenol; 3,4,5-fluorothiophenol; 2,3,4,5-tetrafluorothiophenol; 2,3,5,6-tetrafluorothiophenol; 4-chlorotetrafluorothiophenol; pentachlorothiophenol; 2-chlorothiophenol; 3-chlorothiophenol; 4-chlorothiophenol; 2,3-chlorothiophenol; 2,4-chlorothiophenol; 3,4-chlorothiophenol; 3,5-chlorothiophenol; 2,3,4-chlorothiophenol; 3,4,5-chlorothiophenol; 2,3,4,5-tetrachlorothiophenol; 2,3,5,6-tetrachlorothiophenol; pentabromothiophenol; 2-bromothiophenol; 3-bromothiophenol; 4-bromothiophenol; 2,3-bromothiophenol; 2,4-bromothiophenol; 3,4-bromothiophenol; 3,5-bromothiophenol; 2,3,4-bromothiophenol; 3,4,5-bromothiophenol; 2,3,4,5-tetrabromothiophenol; 2,3,5,6-tetrabromothiophenol; pentaiodothiophenol; 2-iodothiophenol; 3-iodothiophenol; 4-iodothiophenol; 2,3-iodothiophenol; 2,4-iodothiophenol; 3,4-iodothiophenol; 3,5-iodothiophenol; 2,3,4-iodothiophenol; 3,4,5-iodothiophenol; 2,3,4,5-tetraiodothiophenol; 2,3,5,6-tetraiodothiophenol; and their zinc salts. Preferably, the halogenated organosulfur compound is pentachlorothiophenol, which is commercially available in neat form or under the tradename STRUKTOL®, a clay-based carrier containing the sulfur compound pentachlorothiophenol loaded at 45 percent (correlating to 2.4 parts PCIP). STRUKTOL® is commercially available from Struktol Company of America of Stow, Ohio. PCIP is commercially available in neat or salt form from eChinacem of San Francisco, Calif. Most preferably, the halogenated organosulfur compound is the zinc salt of pentachlorothiophenol. The halogenated organosulfur compounds of the present invention are preferably present in an amount greater than about 2.2 pph, more preferably between about 2.3 pph and about 5 pph, and most preferably between about 2.3 and about 4 pph.

Fillers typically include materials such as tungsten, zinc oxide, barium sulfate, silica, calcium carbonate, zinc carbonate, metals, metal oxides and salts, reground (recycled) core material typically ground to about 30 mesh particle), high-Mooney-viscosity rubber reground, UV absorbers, hindered amine light stabilizers, optical brighteners, and the like. Fillers added to one or more portions of the golf ball typically include processing aids or compounds to affect rheological and mixing properties, density-modifying fillers, tear strength, or reinforcement fillers, and the like. The fillers are generally inorganic, and suitable fillers include numerous metals or metal oxides, such as zinc oxide and tin oxide, as well as barium sulfate, zinc sulfate, calcium carbonate, barium carbonate, clay, tungsten, tungsten carbide, an array of silicas, and mixtures thereof. Fillers may also include various foaming agents or blowing agents which may be readily selected by one of ordinary skill in the art. Fillers may include polymeric, ceramic, metal, and glass microspheres may be solid or hollow, and filled or unfilled. Fillers are typically also added to one or more portions of the golf ball to modify the density thereof to conform to uniform golf ball standards. Fillers may also be used to modify the weight of the center or at least one additional layer for specialty balls.

The invention also includes a method to convert the cis-isomer of the polybutadiene resilient polymer component to the trans-isomer during a molding cycle and to form a golf ball. A variety of methods and materials suitable for cis-to-trans conversion have been disclosed in U.S. Pat. No.

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6,162,135 and U.S. application Ser. No. 09/461,736, filed Dec. 16, 1999; U.S. application Ser. No. 09/458,676, filed Dec. 10, 1999; and 09/461,421, filed Dec. 16, 1999, each of which are incorporated herein, in their entirety, by reference.

The materials used in forming either the golf ball center or any portion of the core, in accordance with the invention, may be combined to form a mixture by any type of mixing known to one of ordinary skill in the art. Suitable types of mixing include single pass and multi-pass mixing. Suitable mixing equipment is well known to those of ordinary skill in the art, and such equipment may include a Banbury mixer, a two-roll mill, or a twin screw extruder.

Conventional mixing speeds for combining polymers are typically used. The mixing temperature depends upon the type of polymer components, and more importantly, on the type of free-radical initiator. Suitable mixing speeds and temperatures are well-known to those of ordinary skill in the art, or may be readily determined without undue experimentation.

The mixture can be subjected to, e.g., a compression or injection molding process, to obtain solid spheres for the center or hemispherical shells for forming an intermediate layer. The temperature and duration of the molding cycle are selected based upon reactivity of the mixture. The molding cycle may have a single step of molding the mixture at a single temperature for a fixed time duration. The molding cycle may also include a two-step process, in which the polymer mixture is held in the mold at an initial temperature for an initial duration of time, followed by holding at a second, typically higher temperature for a second duration of time. In a preferred embodiment of the current invention, a single-step cure cycle is employed. The materials used in forming either the golf ball center or any portion of the core, in accordance with the invention, may be combined to form a golf ball by an injection molding process, which is also well-known to one of ordinary skill in the art. Although the curing time depends on the various materials selected, those of ordinary skill in the art will be readily able to adjust the curing time upward or downward based on the particular materials used and the discussion herein.

Properties that are desirable for the cover include good moldability, high abrasion resistance, high tear strength, high resilience, and good mold release. The cover typically has a thickness to provide sufficient strength, good performance characteristics, and durability. The cover preferably has a thickness of less than about 0.1 inches, more preferably, less than about 0.05 inches, and most preferably, between about 0.02 inches and about 0.04 inches. The invention is particularly directed towards a multilayer golf ball which comprises a core, an inner cover layer, and an outer cover layer. In this embodiment, preferably, at least one of the inner and outer cover layer has a thickness of less than about 0.05 inches, more preferably between about 0.02 inches and about 0.04 inches. Most preferably, the thickness of either layer is about 0.03 inches.

When the golf ball of the present invention includes an inner cover layer, this layer can include any materials known to those of ordinary skill in the art, including thermoplastic and thermosetting material, but preferably the inner cover can include any suitable materials, such as ionic copolymers of ethylene and an unsaturated monocarboxylic acid which are available under the trademark SURILYN® of E.I. DuPont de Nemours & Co., of Wilmington, Del., or IOTEX® or ESCOR® of Exxon. These are copolymers or terpolymers of ethylene and methacrylic acid or acrylic acid partially neutralized with salts of zinc, sodium, lithium, magnesium, potassium, calcium, manganese, nickel or the like, in which

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the salts are the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially neutralized and might include methacrylic, crotonic, maleic, fumaric or itaconic acid.

This golf ball can likewise include one or more homopolymeric or copolymeric inner cover materials, such as:

(1) Vinyl resins, such as those formed by the polymerization of vinyl chloride, or by the copolymerization of vinyl chloride with vinyl acetate, acrylic esters or vinylidene chloride;

(2) Polyolefins, such as polyethylene, polypropylene, polybutylene and copolymers such as ethylene methylacrylate, ethylene ethylacrylate, ethylene vinyl acetate, ethylene methacrylic or ethylene acrylic acid or propylene acrylic acid and copolymers and homopolymers produced using a single-site catalyst or a metallocene catalyst;

(3) Polyurethanes, such as those prepared from polyols and diisocyanates or polyisocyanates and those disclosed in U.S. Pat. No. 5,334,673;

(4) Polyureas, such as those disclosed in U.S. Pat. No. 5,484,870;

(5) Polyamides, such as poly(hexamethylene adipamide) and others prepared from diamines and dibasic acids, as well as those from amino acids such as poly(caprolactam), and blends of polyamides with SURLYN®, polyethylene, ethylene copolymers, ethyl-propylene-non-conjugated diene terpolymer, and the like;

(6) Acrylic resins and blends of these resins with poly vinyl chloride, elastomers, and the like;

(7) Thermoplastics, such as urethanes; olefinic thermoplastic rubbers, such as blends of polyolefins with ethylene-propylene-non-conjugated diene terpolymer; block copolymers of styrene and butadiene, isoprene or ethylene-butylene rubber; or copoly(ether-amide), such as PEBAX®, sold by ELF Atochem of Philadelphia, Pa.;

(8) Polyphenylene oxide resins or blends of polyphenylene oxide with high impact polystyrene as sold under the trademark NORYL® by General Electric Company of Pittsfield, Mass.;

(9) Thermoplastic polycesters, such as polyethylene terephthalate, polybutylene terephthalate, polyethylene terephthalate/glycol modified and elastomers sold under the trademarks HYTREL® by E.I. DuPont de Nemours & Co. of Wilmington, Del., and LOMOD® by General Electric Company of Pittsfield, Mass.;

(10) Blends and alloys, including polycarbonate with acrylonitrile butadiene styrene, polybutylene terephthalate, polyethylene terephthalate, styrene maleic anhydride, polyethylene, elastomers, and the like, and polyvinyl chloride with acrylonitrile butadiene styrene or ethylene vinyl acetate or other elastomers; and

(11) Blends of thermoplastic rubbers with polyethylene, propylene, polyacetal, nylon, polyesters, cellulose esters, and the like.

Preferably, the inner cover includes polymers, such as ethylene, propylene, butene-1 or hexane-1 based homopolymers or copolymers including functional monomers, such as acrylic and methacrylic acid and fully or partially neutralized ionomer resins and their blends, methyl acrylate, methyl methacrylate homopolymers and copolymers, imidized, amino group containing polymers, polycarbonate, reinforced polyamides, polyphenylene oxide, high impact polystyrene, polyether ketone, polysulfone, poly(phenylene

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sulfide), acrylonitrile-butadiene, acrylic-styrene-acrylonitrile, poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene vinyl alcohol), poly(tetrafluoroethylene) and their copolymers including functional comonomers, and blends thereof. Suitable cover compositions also include a polyether or polyester thermoplastic urethane, a thermoset polyurethane, a low modulus ionomer, such as acid-containing ethylene copolymer ionomers, including E/X/Y terpolymers where E is ethylene, X is an acrylate or methacrylate-based softening comonomer present in about 0 to 50 weight percent and Y is acrylic or methacrylic acid present in about 5 to 35 weight percent. Preferably, the acrylic or methacrylic acid is present in about 8 to 35 weight percent, more preferably 8 to 25 weight percent, and most preferably 8 to 20 weight percent.

Any of the inner or outer cover layers may also be formed from polymers containing  $\alpha$ ,  $\beta$ -unsaturated carboxylic acid groups, or the salts thereof, that have been 100 percent neutralized by organic fatty acids. The acid moieties of the highly-neutralized polymers ("HNP"), typically ethylene-based ionomers, are preferably neutralized greater than about 70%, more preferably greater than about 90%, and most preferably at least about 100%. The HNP's can be also blended with a second polymer component, which, if containing an acid group, may be neutralized in a conventional manner, by the organic fatty acids of the present invention, or both. The second polymer component, which may be partially or fully neutralized, preferably comprises ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, polyamides, polycarbonates, polyesters, polyurethanes, polyureas, thermoplastic elastomers, polybutadiene rubber, balata, metallocene-catalyzed polymers (grafted and non-grafted), single-site polymers, high-crystalline acid polymers, cationic ionomers, and the like.

The acid copolymers can be described as E/X/Y copolymers where E is ethylene, X is an  $\alpha$ ,  $\beta$ -ethylenically unsaturated carboxylic acid, and Y is a softening comonomer. In a preferred embodiment, X is acrylic or methacrylic acid and Y is a C<sub>1-8</sub> alkyl acrylate or methacrylate ester. X is preferably present in an amount from about 1 to about 35 weight percent of the polymer, more preferably from about 5 to about 30 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer. Y is preferably present in an amount from about 0 to about 50 weight percent of the polymer, more preferably from about 5 to about 25 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer.

The organic acids are aliphatic, mono-functional (saturated, unsaturated, or multi-unsaturated) organic acids. Salts of these organic acids may also be employed. The salts of organic acids of the present invention include the salts of barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, or calcium, salts of fatty acids, particularly stearic, bebenic, erucic, oleic, linoleic or dimerized derivatives thereof. It is preferred that the organic acids and salts of the present invention be relatively non-migratory (they do not bloom to the surface of the polymer under ambient temperatures) and non-volatile (they do not volatilize at temperatures required for melt-blending).

Thermoplastic polymer components, such as copolyetheresters, copolyesteresters, copolyetheramides, elastomeric polyolefins, styrene diene block copolymers and their hydrogenated derivatives, copolyesteramides, thermoplastic polyurethanes, such as copolyetherurethanes,

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copolyesterurethanes, copolyureaurethanes, epoxy-based polyurethanes, polycaprolactone-based polyurethanes, polyureas, and polycarbonate-based polyurethanes fillers, and other ingredients, if included, can be blended in either before, during, or after the acid moieties are neutralized, thermoplastic polyurethanes.

Examples of these materials are disclosed in U.S. patent application Publication Nos. 2001/0018375 and 2001/0019971, which are incorporated herein in their entirety by express reference thereto.

While the outer cover may be formed of any of the above-listed materials, the outer cover preferably includes a polyurethane, polyurea, or epoxy composition, generally comprising the reaction product of at least one polyisocyanate, polyol, and at least one curing agent. Any polyisocyanate available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyisocyanates include, but are not limited to, 4,4'-diphenylmethane diisocyanate ("MDI"); polymeric MDI; carbodiimide-modified liquid MDI; 4,4'-dicyclohexylmethane diisocyanate ("H<sub>12</sub>MDI"); p-phenylene diisocyanate ("PPDI"); m-phenylene diisocyanate ("MPDI"); toluene diisocyanate ("TDI"); 3,3'-dimethyl-4,4'-biphenylene diisocyanate ("TODI"); isophoronediiisocyanate ("IPDI"); hexamethylene diisocyanate ("HDI"); naphthalene diisocyanate ("NDI"); xylene diisocyanate ("XDI"); p-tetramethylxylene diisocyanate ("p-TMXDI"); m-tetramethylxylene diisocyanate ("m-TMXDI"); ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; cyclohexyl diisocyanate; 1,6-hexamethylene-diisocyanate ("HDI"); dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,4,4-trimethyl-1,6-hexane diisocyanate ("TMDI"); tetracene diisocyanate; naphthalene diisocyanate; anthracene diisocyanate; isocyanurate of toluene diisocyanate; uretdione of hexamethylene diisocyanate; and mixtures thereof. Preferably, the polyisocyanate includes MDI, PPDI, TDI, or a mixture thereof, and more preferably, the polyisocyanate includes MDI. It should be understood that, as used herein, the term "MDI" includes 4,4'-diphenylmethane diisocyanate, polymeric MDI, carbodiimide-modified liquid MDI, and mixtures thereof and, additionally, that the diisocyanate employed may be "low free monomer," understood by one of ordinary skill in the art to have lower levels of "free" monomer isocyanate groups, typically less than about 0.1% free monomer groups. Examples of "low free monomer" diisocyanates include, but are not limited to Low Free Monomer MDI, Low Free Monomer TDI, and Low Free Monomer PPDI.

The at least one polyisocyanate should have less than about 14% unreacted NCO groups. Preferably, the at least one polyisocyanate has no greater than about 7.5% NCO, and more preferably, less than about 7.0%. It is well understood in the art that the hardness of polyurethane can be correlated to the percent of unreacted NCO groups (See FIG. 2). As such, if the polyisocyanate has less than about 7.0% unreacted groups, the corresponding polyurethane material will have a material hardness of less than about 50 Shore D.

It should be understood, especially to one of ordinary skill in the art, that there is a fundamental difference between "material hardness" and "hardness, as measured directly on a golf ball." Material hardness is defined by the procedure set forth in ASTM-D2240 and generally involves measuring

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the hardness of a flat "slab" or "button" formed of the material of which the hardness is to be measured. Hardness, when measured directly on a golf ball (or other spherical surface) is a completely different measurement and, therefore, results in a different hardness value. This difference results from a number of factors including, but not limited to, ball construction (i.e., core type, number of core and/or cover layers, etc.), ball (or sphere) diameter, and the material composition of adjacent layers. It should also be understood that the two measurement techniques are not linearly related and, therefore, one hardness value cannot easily be correlated to the other.

Any polyol available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyols include, but are not limited to, polyether polyols, hydroxy-terminated polybutadiene (including partially/fully hydrogenated derivatives), polyester polyols, polycaprolactone polyols, and polycarbonate polyols. In one preferred embodiment, the polyol includes polyether polyol. Examples include, but are not limited to, polytetramethylene ether glycol ("PTMEG"), polyethylene propylene glycol, polyoxypropylene glycol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds and substituted or unsubstituted aromatic and cyclic groups. Preferably, the polyol of the present invention includes PTMEG.

Suitable polyester polyols include, but are not limited to, polyethylene adipate glycol; polybutylene adipate glycol; polyethylene propylene adipate glycol; o-phthalate-1,6-hexanediol; poly(hexamethylene adipate) glycol; and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

Suitable polycaprolactone polyols include, but are not limited to, 1,6-hexanediol-initiated polycaprolactone, diethylene glycol initiated polycaprolactone, trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, PTMEG-initiated polycaprolactone, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

Suitable polycarbonates include, but are not limited to, polyphthalate carbonate and poly(hexamethylene carbonate) glycol. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

Polyamine curatives are also suitable for use in polyurethane covers. Preferred polyamine curatives include, but are not limited to, 3,5-dimethylthio-2,4-toluenediamine and isomers thereof; 3,5-diethyltoluene-2,4-diamine and isomers thereof, such as 3,5-diethyltoluene-2,6-diamine; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline) ("MCDEA"); polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkyldiamino diphenyl methane; p,p'-methylene dianiline ("MDA"); m-phenylenediamine ("MPDA"); 4,4'-methylene-bis-(2-chloroaniline) ("MOCA"); 4,4'-methylene-bis-(2,6-diethylaniline) ("MDEA"); 4,4'-methylene-bis-(2,3-dichloroaniline) ("MDCA"); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenylmethane; trimethylene glycol di-p-aminobenzoate; and mixtures thereof. Preferably, the curing agent of the present invention includes 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, such as Ethacure® 300, commercially available

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from Albermarle Corporation of Baton Rouge, La. Suitable polyamine curatives include both primary and secondary amines.

At least one of a diol, triol, tetraol, or hydroxy-terminated curatives may be added to the aforementioned polyurethane composition. Suitable diol, triol, and tetraol groups include ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy)benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-( $\beta$ -hydroxyethyl)ether; hydroquinone-di-( $\beta$ -hydroxyethyl)ether; and mixtures thereof. Preferred hydroxy-terminated curatives include 1,3-bis(2-hydroxyethoxy)benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene; 1,4-butanediol, and mixtures thereof.

Both the hydroxy-terminated and amine curatives can include one or more saturated, unsaturated, aromatic, and cyclic groups. Additionally, the hydroxy-terminated and amine curatives can include one or more halogen groups. The polyurethane composition can be formed with a blend or mixture of curing agents. If desired, however, the polyurethane composition may be formed with a single curing agent.

In a particularly preferred embodiment of the present invention, saturated polyurethanes used to form cover layers, preferably the outer cover layer, and may be selected from among both castable thermoset and thermoplastic polyurethanes. In this embodiment, the saturated polyurethanes are substantially free of aromatic groups or moieties.

Saturated diisocyanates which can be used include, but are not limited to, ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene-diisocyanate; 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; dicyclohexylmethane diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isophorone diisocyanate ("IPDI"); methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate ("TMDI"). The most preferred saturated diisocyanates are 4,4'-dicyclohexylmethane diisocyanate and isophorone diisocyanate ("IPDI").

Saturated polyols which are appropriate for use in this invention include, but are not limited to, polycether polyols such as polytetramethylene ether glycol and poly(oxypropylene) glycol. Suitable saturated polyester polyols include polyethylene adipate glycol, polyethylene propylene adipate glycol, polybutylene adipate glycol, polycarbonate polyol and ethylene oxide-capped polyoxypropylene diols. Saturated polycaprolactone polyols which are useful in the invention include diethylene glycol initiated polycaprolactone, 1,4-butanediol initiated polycaprolactone, 1,6-hexanediol initiated polycaprolactone; trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, PTMEG-initiated polycaprolactone. The most preferred saturated polyols are PTMEG and PTMEG-initiated polycaprolactone.

Suitable saturated curatives include 1,4-butanediol, ethylene glycol, diethylene glycol, polytetramethylene ether glycol, propylene glycol; trimethanolpropane; tetra-(2-hydroxypropyl)-ethylenediamine; isomers and mixtures of isomers of cyclohexyldimethylol, isomers and mixtures of

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isomers of cyclohexane bis(methylamine); triisopropanolamine, ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, 4,4'-dicyclohexylmethane diamine, 2,2,4-trimethyl-1,6-hexanediolamine; 2,4,4-trimethyl-1,6-hexanediolamine; diethyleneglycol di-(aminopropyl)ether; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,2-bis-(sec-butylamino)cyclohexane; 1,4-bis-(sec-butylamino)cyclohexane; isophorone diamine, hexamethylene diamine, propylene diamine, 1-methyl-2,4-cyclohexyl diamine, 1-methyl-2,6-cyclohexyl diamine, 1,3-diaminopropane, dimethylamino propylamine, diethylamino propylamine, imido-bis-propylamine, isomers and mixtures of isomers of diaminocyclohexane, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, and diisopropanolamine. The most preferred saturated curatives are 1,4-butanediol, 1,4-cyclohexyldimethylol and 4,4'-bis-(sec-butylamino)-dicyclohexylmethane.

Suitable catalysts include, but are not limited to bismuth catalyst, oleic acid, triethylenediamine (DABCO®-33LV), di-butyltin dilaurate (DABCO®-T12) and acetic acid. The most preferred catalyst is di-butyltin dilaurate (DABCO®-T12). DABCO® materials are manufactured by Air Products and Chemicals, Inc.

It is well known in the art that if the saturated polyurethane materials are to be blended with other thermoplastics, care must be taken in the formulation process so as to produce an end product which is thermoplastic in nature. Thermoplastic materials may be blended with other thermoplastic materials, but thermosetting materials are difficult if not impossible to blend homogeneously after the thermosetting materials are formed. Preferably, the saturated polyurethane comprises from about 1 to about 100%, more preferably from about 10 to about 75% of the cover composition and/or the intermediate layer composition. About 90 to about 10%, more preferably from about 90 to about 25% of the cover and/or the intermediate layer composition is comprised of one or more other polymers and/or other materials as described below. Such polymers include, but are not limited to polyurethane/polyurea ionomers, polyurethanes or polyureas, epoxy resins, polyethylenes, polyamides and polyesters, polycarbonates and polyacrylin. Unless otherwise stated herein, all percentages are given in percent by weight of the total composition of the golf ball layer in question.

Polyurethane prepolymers are produced by combining at least one polyol, such as a polyether, polycaprolactone, polycarbonate or a polyester, and at least one isocyanate. Thermosetting polyurethanes are obtained by curing at least one polyurethane prepolymer with a curing agent selected from a polyamine, triol or tetraol. Thermoplastic polyurethanes are obtained by curing at least one polyurethane prepolymer with a diol curing agent. The choice of the curatives is critical because some urethane elastomers that are cured with a diol and/or blends of diols do not produce urethane elastomers with the impact resistance required in a golf ball cover. Blending the polyamine curatives with diol cured urethane elastomeric formulations leads to the production of the thermoset urethanes with improved impact and cut resistance.

Thermoplastic polyurethanes may be blended with suitable materials to produce a thermoplastic end product. Examples of such additional materials may include ionomers such as the SURLYN®, ESCOR® and IOTEK® copolymers described above.

Other suitable materials which may be combined with the saturated polyurethanes in forming the cover and/or inter-

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mediate layer(s) of the golf balls of the invention include ionic or non-ionic polyurethanes and polyureas, epoxy resins, polyethylenes, polyamides and polyesters. For example, the cover and/or intermediate layer may be formed from a blend of at least one saturated polyurethane and thermoplastic or thermoset ionic and non-ionic urethanes and polyurethanes, cationic urethane ionomers and urethane epoxies, ionic and non-ionic polyureas and blends thereof. Examples of suitable urethane ionomers are disclosed in U.S. Pat. No. 5,692,974, the disclosure of which is hereby incorporated by reference in its entirety. Other examples of suitable polyurethanes are described in U.S. Pat. No. 5,334,673. Examples of appropriate polyureas are discussed in U.S. Pat. No. 5,484,870 and examples of suitable polyurethanes cured with epoxy group containing curing agents are disclosed in U.S. Pat. No. 5,908,358, the disclosures of which are hereby incorporated herein by reference in their entirety.

A variety of conventional components can be added to the cover compositions of the present invention. These include, but are not limited to, white pigment such as  $\text{TiO}_2$ ,  $\text{ZnO}$ , optical brighteners, surfactants, processing aids, foaming agents, density-controlling fillers, UV stabilizers and light stabilizers. Saturated polyurethanes are resistant to discoloration. However, they are not immune to deterioration in their mechanical properties upon weathering. Addition of UV absorbers and light stabilizers to any of the above compositions and, in particular, the polyurethane compositions, help to maintain the tensile strength, elongation, and color stability. Suitable UV absorbers and light stabilizers include TINUVIN® 328, TINUVIN® 213, TINUVIN® 765, TINUVIN® 770 and TINUVIN® 622. The preferred UV absorber is TINUVIN® 328, and the preferred light stabilizer is TINUVIN® 765. TINUVIN® products are available from Ciba-Geigy. Dyes, as well as optical brighteners and fluorescent pigments may also be included in the golf ball covers produced with polymers formed according to the present invention. Such additional ingredients may be added in any amounts that will achieve their desired purpose.

Any method known to one of ordinary skill in the art may be used to polyurethanes of the present invention. One commonly employed method, known in the art as a one-shot method, involves concurrent mixing of the polyisocyanate, polyol, and curing agent. This method results in a mixture that is inhomogeneous (more random) and affords the manufacturer less control over the molecular structure of the resultant composition. A preferred method of mixing is known as a prepolymer method. In this method, the polyisocyanate and the polyol are mixed separately prior to addition of the curing agent. This method affords a more homogeneous mixture resulting in a more consistent polymer composition. Other methods suitable for forming the layers of the present invention include reaction injection molding ("RIM"), liquid injection molding ("LIM"), and pre-reacting the components to form an injection moldable thermoplastic polyurethane and then injection molding, all of which are known to one of ordinary skill in the art.

It has been found by the present invention that the use of a castable, reactive material, which is applied in a fluid form, makes it possible to obtain very thin outer cover layers on golf balls. Specifically, it has been found that castable, reactive liquids, which react to form a urethane elastomer material, provide desirable very thin outer cover layers.

The castable, reactive liquid employed to form the urethane elastomer material can be applied over the core using a variety of application techniques such as spraying,

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dipping, spin coating, or flow coating methods which are well known in the art. An example of a suitable coating technique is that which is disclosed in U.S. Pat. No. 5,733,428, the disclosure of which is hereby incorporated by reference in its entirety in the present application.

The outer cover is preferably formed around the inner cover by mixing and introducing the material in the mold halves. It is important that the viscosity be measured over time, so that the subsequent steps of filling each mold half, introducing the core into one half and closing the mold can be properly timed for accomplishing centering of the core cover halves fusion and achieving overall uniformity. Suitable viscosity range of the curing urethane mix for introducing cores into the mold halves is determined to be approximately between about 2,000 cP and about 30,000 cP, with the preferred range of about 8,000 cP to about 15,000 cP.

To start the cover formation, mixing of the prepolymer and curative is accomplished in motorized mixer including mixing head by feeding through lines metered amounts of curative and prepolymer. Top preheated mold halves are filled and placed in fixture units using centering pins moving into holes in each mold. At a later time, a bottom mold half or a series of bottom mold halves have similar mixture amounts introduced into the cavity. After the reacting materials have resided in top mold halves for about 40 to about 80 seconds, a core is lowered at a controlled speed into the gelling reacting mixture.

A ball cup holds the ball core through reduced pressure (or partial vacuum). Upon location of the coated core in the halves of the mold after gelling for about 40 to about 80 seconds, the vacuum is released allowing core to be released. The mold halves, with core and solidified cover half thereon, are removed from the centering fixture unit, inverted and mated with other mold halves which, at an appropriate time earlier, have had a selected quantity of reacting polyurethane prepolymer and curing agent introduced therein to commence gelling.

Similarly, U.S. Pat. No. 5,006,297 and U.S. Pat. No. 5,334,673 both also disclose suitable molding techniques which may be utilized to apply the castable reactive liquids employed in the present invention. Further, U.S. Pat. Nos. 6,180,040 and 6,180,722 disclose methods of preparing dual core golf balls. The disclosures of these patents are hereby incorporated by reference in their entirety. However, the method of the invention is not limited to the use of these techniques.

In one embodiment of the golf ball of the present invention, the center has a first hardness, the outer core layer has a second hardness greater than the first, and the inner cover layer has a third hardness greater than the second. Additionally, it is preferred that the outer cover layer has a fourth hardness less than the third hardness.

The molding process and composition of golf ball portions typically results in a gradient of material properties. Methods employed in the prior art generally exploit hardness to quantify these gradients. Hardness is a qualitative measure of static modulus and does not represent the modulus of the material at the deformation rates associated with golf ball use, i.e., impact by a club. As is well known to one skilled in the art of polymer science, the time-temperature superposition principle may be used to emulate alternative deformation rates. For golf ball portions including polybutadiene, a 1-Hz oscillation at temperatures between 0° C. and -50° C. are believed to be qualitatively equivalent to golf ball impact rates. Therefore, measurement of loss tangent and dynamic stiffness at 0° C. to -50° C. may be

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used to accurately anticipate golf ball performance, preferably at temperatures between about -20° C. and -50° C.

The resultant golf balls typically have a coefficient of restitution of greater than about 0.7, preferably greater than about 0.75, and more preferably greater than about 0.78. The golf balls also typically have an Atti compression of at least about 40, preferably from about 50 to 120, and more preferably from about 60 to 100. The golf ball cured polybutadiene material typically has a hardness of at least about 15 Shore A, preferably between about 30 Shore A and 80 Shore D, more preferably between about 50 Shore A and 60 Shore D.

When golf balls are prepared according to the invention, they typically will have dimple coverage greater than about 60 percent, preferably greater than about 65 percent, and more preferably greater than about 75 percent. The flexural modulus of the cover on the golf balls, as measured by ASTM method D6272-98, Procedure B, is typically greater than about 500 psi, and is preferably from about 500 psi to 150,000 psi. As discussed herein, the outer cover layer is preferably formed from a relatively soft polyurethane material. In particular, the material of the outer cover layer should have a material hardness, as measured by ASTM-D2240, less than about 60 Shore D, more preferably between about 25 and about 50 Shore D, and most preferably between about 45 and about 48 Shore D. The inner cover layer preferably has a material hardness of less than about 70 Shore D, more preferably between about 30 and about 70 Shore D, and most preferably, between about 50 and about 65 Shore D.

The core of the present invention has a Soft Center Deflection Index ("SCDI") compression of less than about 160, more preferably, between about 40 and about 160, and most preferably, between about 60 and about 120. In an alternative, low compression embodiment, the core has an Atti compression less than about 20, more preferably less than about 10, and most preferably, 0.

The SCDI is a program change for the Dynamic Compression Machine ("DCM") that allows determination of the pounds required to deflect a core 10% of its diameter. The DCM is an apparatus that applies a load to a core or ball and measures the number of inches the core or ball is deflected at measured loads. A crude load/deflection curve is generated that is fit to the Atti compression scale that results in a number being generated that represents an Atti compression. The DCM does this via a load cell attached to the bottom of a hydraulic cylinder that is triggered pneumatically at a fixed rate (typically about 1.0 ft/s) towards a stationary core.

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Attached to the cylinder is an LVDT that measures the distance the cylinder travels during the testing timeframe. A software-based logarithmic algorithm ensures that measurements are not taken until at least five successive increases in load are detected during the initial phase of the test.

The SCDI is a slight variation of this set up. The hardware is the same, but the software and output has changed. With the SCDI, we are only interested in the pounds of force required to deflect a core a amount of inches. That amount of deflection is 10% percent of the core's diameter. The DCM is triggered, the cylinder deflects the core by 10% of its diameter, and the DCM reports back the pounds of force required (as measured from the attached load cell) to deflect the core by that amount. The value displayed is a single number in units of pounds.

The overall outer diameter ("OD") of the core is less than about 1.610 inches, preferably, no greater than 1.590 inches, more preferably between about 1.540 inches and about 1.580 inches, and most preferably between about 1.50 inches to about 1.570 inches. The OD of the inner cover layer is preferably between 1.580 inches and about 1.640 inches, more preferably between about 1.590 inches to about 1.630 inches, and most preferably between about 1.600 inches to about 1.630 inches.

The present multilayer golf ball can have an overall diameter of any size. Although the United States Golf Association ("USGA") specifications limit the minimum size of a competition golf ball to 1.680 inches. There is no specification as to the maximum diameter. Golf balls of any size, however, can be used for recreational play. The preferred diameter of the present golf balls is from about 1.680 inches to about 1.800 inches. The more preferred diameter is from about 1.680 inches to about 1.760 inches. The most preferred diameter is about 1.680 inches to about 1.740 inches.

#### EXAMPLE

Three solid cores, each having an outer diameter of 1.58 inches, were formed of a composition comprising polybutadiene rubber, zinc diacrylate, zinc oxide, dicumyl peroxide, barium sulfate, and color dispersion. One core, representative of conventional technology, was used as a control. The two remaining cores were each additionally blended with 5.3 parts Struktol® (Example 1) and the zinc salt of pentachlorothiophenol at 2.4 parts (Example 2). Struktol® at 5.3 parts contains 2.4 parts PCTP. The specific compositions for each of the solid cores are presented below in Table I.

TABLE I

	CONTROL			EXAMPLE 1			EXAMPLE 2		
INGREDIENT									
polybutadiene rubber	100	100	100	100	100	100	100	100	100
zinc diacrylate	18	25	30	27	34	41	20	25	30
dicumyl peroxide	0.5	0.5	0.5	1.8	1.8	1.8	0.8	0.8	0.8
Struktol® A95	—	—	—	5.3	5.3	5.3	—	—	—
zinc salt of PCTP	—	—	—	—	—	—	2.4	2.4	2.4
zinc oxide	26.5	24.1	22.2	5	5	5	5	5	5
barium sulfate	—	—	—	16.2	13.4	10.6	21.7	19.7	17.7
color dispersion	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14
PROPERTY									
Effective Modulus (psi)	3800	6200	8700	4100	6200	7700	3600	5100	7400
Atti Compression	17	52	76	22	52	67	13	38	65
COR @ 125 ft/s	0.764	0.789	0.802	0.773	0.794	0.802	0.782	0.801	0.813

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It is very apparent that the addition of PCTP, in either form, increases COR, decreases compression, or both. In particular, the PCTP zinc salt (Example 2) provides comparable COR's with lower compression and/or increased COR's with comparable (or lower) compression, both of which are desirable golf ball properties.

The halogenated organosulfur polymers of the present invention may also be used in golf equipment, in particular, inserts for golf clubs, such as putters, irons, and woods, and in golf shoes and components thereof.

As used herein, the term "about," used in connection with one or more numbers or numerical ranges, should be understood to refer to all such numbers, including all numbers in a range.

The invention described and claimed herein is not to be limited in scope by the specific embodiments herein disclosed, since these embodiments are intended as illustrations of several aspects of the invention. Any equivalent embodiments are intended to be within the scope of this invention. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

What is claimed is:

1. A golf ball comprising a core and a cover disposed about the core, wherein the core comprises a center and an outer core layer, and the cover comprises an inner cover layer and an outer cover layer; and

wherein the center has an outer diameter from about 0.375 inches to about 1.4 inches, a deflection of greater than about 4.5 mm under a load of 100 Kg, and comprises polybutadiene having a polydispersity of about 2 or less;

the outer core layer has an outer diameter of from about 1.4 inches to about 1.62 inches;

the inner cover layer is harder than both the outer core layer and the center, having an outer diameter of greater than about 1.58 inches and a material hardness of between about 60 and about 72 Shore D; and

the outer cover layer has a hardness of greater than about 50 Shore D and a material hardness of less than about 50 Shore D and comprises a thermosetting polyurethane composition comprising a polyisocyanate having less than about 7.0% unreacted NCO groups.

2. The golf ball of claim 1, wherein the inner cover layer outer diameter is from about 1.59 inches to about 1.66 inches.

3. The golf ball of claim 1, wherein the center has an outer diameter between about 0.5 inches and about 1.25 inches.

4. The golf ball of claim 3, wherein the center has an outer diameter no greater than about 1.0 inches.

5. The golf ball of claim 1, wherein the outer core layer outer diameter is from about 1.52 inches to about 1.58 inches.

6. The golf ball of claim 1, wherein the outer cover layer is softer than the inner cover layer.

7. The golf ball of claim 1, wherein the center is solid, liquid, hollow, or air-filled.

8. The golf ball of claim 1, wherein at least one of the inner or outer cover layers have a thickness of less than about 0.05 inches.

9. The golf ball of claim 1, wherein the inner cover layer comprises an ionomeric material, vinyl resins, polyolefins, polyurethanes, polyureas, polyamides, acrylic resins, thermoplastics, polyphenylene oxide resins, thermoplastic

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polyesters, thermoplastic rubbers, fully-neutralized polymers, partially-neutralized polymers, and mixtures thereof.

10. The golf ball of claim 1, wherein at least one of the center and the outer core layer comprises between 2.4 parts and about 5 parts of a halogenated organosulfur compound.

11. The golf ball of claim 10, wherein the halogenated organosulfur compound is selected from the group consisting of pentafluorothiophenol; 2-fluorothiophenol; 3-fluorothiophenol; 4-fluorothiophenol; 2,3-fluorothiophenol; 2,4-fluorothiophenol; 3,4-fluorothiophenol; 3,5-fluorothiophenol; 2,3,4-fluorothiophenol; 3,4,5-fluorothiophenol; 2,3,4,5-tetrafluorothiophenol; 2,3,5,6-tetrafluorothiophenol; 4-chlorotetrafluorothiophenol; pentachlorothiophenol; 2-chlorothiophenol; 3-chlorothiophenol; 4-chlorothiophenol; 2,3-chlorothiophenol; 2,4-chlorothiophenol; 3,4-chlorothiophenol; 3,5-chlorothiophenol; 2,3,4-chlorothiophenol; 3,4,5-chlorothiophenol; 2,3,4,5-tetrachlorothiophenol; 2,3,5,6-tetrachlorothiophenol; pentabromothiophenol; 2-bromothiophenol; 3-bromothiophenol; 4-bromothiophenol; 2,3-bromothiophenol; 2,4-bromothiophenol; 3,4-bromothiophenol; 3,5-bromothiophenol; 2,3,4-bromothiophenol; 3,4,5-bromothiophenol; 2,3,4,5-tetrabromothiophenol; 2,3,5,6-tetrabromothiophenol; pentaiodothiophenol; 2-iodothiophenol; 3-iodothiophenol; 4-iodothiophenol; 2,3-iodothiophenol; 2,4-iodothiophenol; 3,4-iodothiophenol; 3,5-iodothiophenol; 2,3,4-iodothiophenol; 3,4,5-iodothiophenol; 2,3,4,5-tetraiodothiophenol; 2,3,5,6-tetraiodothiophenol; and their zinc salts, the metal salts thereof, and mixtures thereof.

12. The golf ball of claim 10, wherein the halogenated organosulfur compound is pentachlorothiophenol, the zinc salt thereof, the calcium salt thereof, or the magnesium salt thereof.

13. The golf ball of claim 11, wherein the metal salt is selected from the group consisting of zinc, calcium, magnesium, sodium, and lithium.

14. The golf ball of claim 10, wherein the center and the outer core layer are solid and the center comprises the halogenated organosulfur compound.

15. The golf ball of claim 10, wherein the center and the outer core layer are solid and the outer core layer comprises the halogenated organosulfur compound.

16. The golf ball of claim 1, wherein the core has an SCDI compression less than about 160.

17. The golf ball of claim 1, wherein the core has an SCDI compression between about 60 and about 120.

18. The golf ball of claim 1, wherein the thermosetting polyurethane composition is saturated.

19. The golf ball of claim 1, wherein at least one of the inner and outer cover layers comprises a polybutadiene rubber composition comprising about 2.2 parts to about 5 parts of a halogenated organosulfur compound.

20. The golf ball of claim 1, wherein the outer core layer is a wound layer.

21. A golf ball comprising a core and a cover disposed about the core, wherein the core comprises a center and an outer core layer, and the cover comprises an inner cover layer and an outer cover layer; and

wherein the center has an outer diameter from about 0.375 inches to about 1.4 inches, a deflection of greater than about 4.5 mm under a load of 100 Kg, and comprises polybutadiene having a polydispersity of about 2 or less;

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the outer core layer has an outer diameter of from about 1.4 inches to about 1.62 inches;

the inner cover layer is harder than both the outer core layer and the center, having an outer diameter of greater than about 1.58 inches and a material hardness of between about 60 and about 72 Shore D;

the outer cover layer has a hardness of greater than about 50 Shore D and a material hardness of less than about 50 Shore D; and

the center has a first hardness, the outer core layer has a second hardness greater than the first.

22. A golf ball comprising a core and a cover disposed about the core, wherein the core comprises a center and an outer core layer, and the cover comprises an inner cover layer and an outer cover layer; and

wherein the center has an outer diameter from about 0.375 inches to about 1.4 inches, a deflection of greater than

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about 4.5 mm under a load of 100 Kg, and comprises polybutadiene having a polydispersity of about 2 or less;

the outer core layer has an outer diameter of from about 1.4 inches to about 1.62 inches;

the inner cover layer is harder than both the outer core layer and the center, having an outer diameter of greater than about 1.58 inches and a material hardness of between 60 and about 72 Shore D;

the outer cover layer has a hardness of greater than about 50 Shore D and a material hardness of less than about 50 Shore D and

at least one of the inner and outer cover layers comprises a thermoplastic or thermosetting polyurea composition.

\* \* \* \* \*

# Exhibit 13



US006960630B2

(12) **United States Patent**  
**Cavallaro et al.**

(10) Patent No.: **US 6,960,630 B2**(45) Date of Patent: **Nov. 1, 2005**

(54) **THIN, THERMOSET,  
POLYURETHANE-COVERED GOLF BALL  
WITH A DUAL CORE**

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(60) Division of application No. 10/051,715, filed on Jan. 17, 2002, now Pat. No. 6,849,006, which is a continuation-in-part of application No. 09/951,963, filed on Sep. 13, 2001, now Pat. No. 6,635,716, and a continuation-in-part of application No. 09/782,782, filed on Feb. 13, 2001, which is a continuation-in-part of application No. 09/274,015, filed on Mar. 22, 1999, now abandoned, which is a continuation-in-part of application No. 08/863,788, filed on May 27, 1997, now Pat. No. 5,885,172, said application No. 10/051,715, is a continuation-in-part of application No. 09/721,740, filed on Nov. 27, 2000, now Pat. No. 6,486,261, which is a continuation-in-part of application No. 09/461,736, filed on Dec. 16, 1999, now Pat. No. 6,465,578, and a continuation-in-part of application No. 09/311,591, filed on May 14, 1999, now Pat. No. 6,210,294.

(51) Int. Cl.<sup>7</sup> ..... **A63B 37/12**

(52) U.S. Cl. .... **525/261; 473/373; 473/374;**  
473/376

(58) Field of Search ..... **525/261; 473/373,**  
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(57) **ABSTRACT**

A golf ball comprising a core including a center having an outer diameter from about 0.375 inches to about 1.4 inches and deflection of greater than about 4.5 mm under a load of 100 Kg and an outer core layer having an outer diameter of from about 1.4 in to about 1.62 in, wherein at least one of the center or core layer includes polybutadiene rubber composition including a halogenated organosulfur compound or a metal salt thereof, and a cover including an inner cover layer having an outer diameter of greater than about 1.58 in and a material hardness of less than about 72 Shore D and an outer cover layer having a hardness of greater than about 50 Shore D and a material hardness of less than about 50 Shore D.

20 Claims, 1 Drawing Sheet

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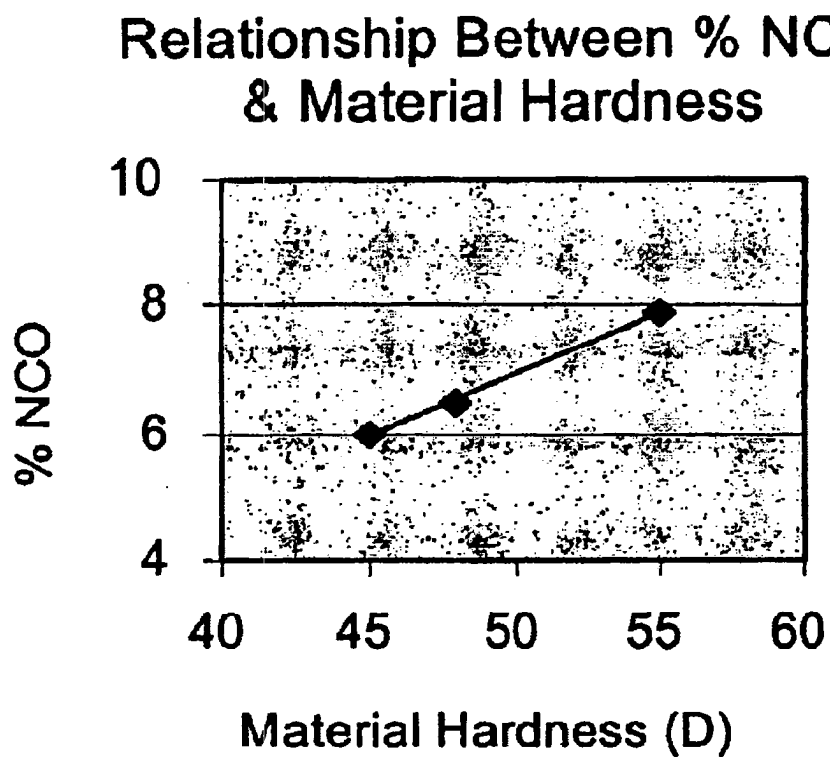
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**FIGURE 1**

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# THIN, THERMOSET, POLYURETHANE-COVERED GOLF BALL WITH A DUAL CORE

## CROSS REFERENCE TO RELATED APPLICATIONS

This application is a divisional of application Ser. No. 10/051,715, filed Jan. 17, 2002, now U.S. Pat. No. 6,849,006. Application Ser. No. 10/051,715 is 1) a continuation-in-part of application Ser. No. 09/951,963, filed Sep. 13, 2001, now U.S. Pat. No. 6,635,716; as well as 2) a continuation-in-part of application Ser. No. 09/782,782, filed Feb. 13, 2001, which is a continuation-in-part of application Ser. No. 09/274,015, filed Mar. 22, 1999 now abandoned, which is a continuation-in-part of application Ser. No. 08/863,788 filed May 27, 1997 now U.S. Pat. No. 5,885,172; and 2a) a continuation-in-part of application Ser. No. 09/721,740, filed Nov. 27, 2000, now U.S. Pat. No. 6,486,261 which is a continuation-in-part of application Ser. No. 09/311,591 filed May 14, 1999 now U.S. Pat. No. 6,210,294, and of 2b) application Ser. No. 09/461,736, filed Dec. 16, 1999, now U.S. Pat. No. 6,465,578 each of which is incorporated herein in its entirety by reference.

## FIELD OF THE INVENTION

This invention relates generally to golf balls, and more specifically, to multi-layer golf balls. In particular, this invention relates to a golf ball having a core including a center and an outer core layer, and a cover including an inner cover layer and an outer cover layer.

## BACKGROUND

Conventional golf balls can be divided into two general classes: solid and wound. Solid golf balls include one-piece, two-piece (i.e., solid core and a cover), and multi-layer (i.e., solid core of one or more layers and/or a cover of one or more layers) golf balls. Wound golf balls typically include a solid, hollow, or fluid-filled center, surrounded by a tensioned elastomeric material, and a cover. Solid balls have traditionally been considered longer and more durable than wound balls, but also lack a particular "feel" provided by the wound construction.

By altering ball construction and composition, manufacturers can vary a wide range of playing characteristics, such as compression, velocity, and spin, each of which can be optimized for various playing abilities. One golf ball component, in particular, that many manufacturers are continually looking to improve is the center or core. The core becomes the "engine" of the golf ball when hit with a club head. Generally, golf ball cores and/or centers are constructed with a polybutadiene-based polymer composition. Compositions of this type are constantly being altered in an effort to provide a higher coefficient of restitution ("COR") while at the same time resulting in a lower compression which, in turn, can lower the golf ball spin rate, provide better "feel," or both. This is a difficult task, however, given the physical limitations of currently-available polymers. As such, there remains a need for novel and improved golf ball core compositions.

It has been determined that, upon addition of a halogenated organosulfur compound or the salts thereof, in particular, pentachlorothiophenol ("PCTP") salt, to polybutadiene rubber compositions, that golf ball cores may be constructed that exhibit increased COR, decreased compression, or both. The present invention is, therefore,

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directed to golf ball centers and cores that include a halogenated organosulfur compound, or a salt thereof, for embodiments such as these.

## SUMMARY OF THE INVENTION

The present invention is directed to a golf ball comprising a core and a cover disposed about the core, wherein the core comprises a center and an outer core layer, and the cover comprises an inner cover layer and an outer cover layer; and wherein the center has an outer diameter from about 0.375 inches to about 1.4 inches and deflection of greater than about 4.5 mm under a load of 100 Kg; the outer core layer has an outer diameter of from about 1.4 in to about 1.62 in; the inner cover layer has an outer diameter of greater than about 1.58 in and a material hardness of less than about 72 Shore D; and the outer cover layer has a hardness of greater than about 50 Shore D and a material hardness of less than about 50 Shore D.

Preferably, the inner cover layer material hardness is between about 60 and about 70 Shore D, and has an outer diameter is from about 1.59 in to about 1.66 inches. The center should have an outer diameter between about 0.5 inches and about 1.25 inches but in a preferred embodiment, the center has an outer diameter no greater than about 1.0 inches. The outer core layer outer has a diameter from about 1.52 inches to about 1.58 inches but in one embodiment, the outer core layer has an outer diameter of at least about 1.55 inches.

In an alternative embodiment, the center has a first hardness, the outer core layer has a second hardness greater than the first, and the inner cover layer has a third hardness greater than the second. Preferably, the outer cover layer has a fourth hardness less than the third hardness.

The center may be solid, liquid, hollow, or air-filled. At least one of the inner or outer cover layers has a thickness of less than about 0.05 inches. The inner cover layer can include an ionomeric material, vinyl resins, polyolefins, polyurethanes, polyureas, polyamides, acrylic resins, thermoplastics, polyphenylene oxide resins, thermoplastic polyesters, thermoplastic rubbers, fully-neutralized polymers, partially-neutralized polymers, and mixtures thereof.

At least one of the center, core layer, or inner and outer cover layers includes polybutadiene rubber composition comprising between about 2.2 parts and about 5 parts of a halogenated organosulfur compound. Suitable halogenated organosulfur compounds include pentafluorothiophenol; 2-fluorothiophenol; 3-fluorothiophenol; 4-fluorothiophenol; 2,3-fluorothiophenol; 2,4-fluorothiophenol; 3,4-fluorothiophenol; 3,5-fluorothiophenol; 2,3,4-fluorothiophenol; 3,4,5-fluorothiophenol; 2,3,4,5-tetrafluorothiophenol; 2,3,5,6-tetrafluorothiophenol; 4-chlorotetrafluorothiophenol; pentachlorothiophenol; 2-chlorothiophenol; 3-chlorothiophenol; 4-chlorothiophenol; 2,3-chlorothiophenol; 2,4-chlorothiophenol; 3,4-chlorothiophenol; 3,5-chlorothiophenol; 2,3,4-chlorothiophenol; 3,4,5-chlorothiophenol; 2,3,4,5-tetrachlorothiophenol; 2,3,5,6-tetrachlorothiophenol; pentabromothiophenol; 2-bromothiophenol; 3-bromothiophenol; 4-bromothiophenol; 2,3-bromothiophenol; 2,4-bromothiophenol; 3,4-bromothiophenol; 3,5-bromothiophenol; 2,3,4-bromothiophenol; 3,4,5-bromothiophenol; 2,3,4,5-tetrabromothiophenol; 2,3,5,6-tetrabromothiophenol; pentaiodothiophenol; 2-iodothiophenol; 3-iodothiophenol; 4-iodothiophenol; 2,3-

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iodothiophenol; 2,4-iodothiophenol; 3,4-iodothiophenol; 3,5-iodothiophenol; 2,3,4-iodothiophenol; 3,4,5-iodothiophenol; 2,3,4,5-tetraiodothiophenol; 2,3,5,6-tetraiodothiophenol; and their zinc salts, the metal salts thereof, and mixtures thereof.

Preferably, the halogenated organosulfur compound is pentachlorothiophenol or the metal salt thereof, the metal salt is selected from the group consisting of zinc, calcium, magnesium, sodium, and lithium. Most preferably, the metal salt is zinc.

In one embodiment, the center and the outer core layer are solid and comprise polybutadiene rubber composition comprising between about 2.2 parts and about 5 parts of a halogenated organosulfur compound or the zinc salt thereof. In a preferred embodiment, the center and the outer core layer are solid and the center comprises polybutadiene rubber composition comprising between about 2.2 parts and about 5 parts of a halogenated organosulfur compound or the zinc salt thereof. In an alternative embodiment, the center and the outer core layer are solid and the outer core layer comprises polybutadiene rubber composition comprising between about 2.2 parts and about 5 parts of a halogenated organosulfur compound or the zinc salt thereof.

The core should have an SCDI compression less than about 160. Preferably, the core has an SCDI compression between about 40 and about 160 and most preferably, the core has an SCDI-compression between about 60 and about 120.

The polybutadiene composition can further include an  $\alpha,\beta$ -unsaturated carboxylic acid or a metal salt thereof, an organic peroxide, and a filler. The outer cover layer may include a polyurethane composition comprising a prepolymer formed of a polyisocyanate and a polyol, and a curing agent. Preferably, at least one of the prepolymer and curing agent are saturated. In an additional embodiment, the polyurethane composition comprises at least one of a UV absorber, a hindered amine light stabilizer, or an optical brightener.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plot of % NCO v. material hardness.

#### DETAILED DESCRIPTION

The golf ball cores of the present invention may comprise any of a variety of constructions, but preferably include a core formed of a center and at least one outer core layer and a cover formed of an outer cover layer and at least one inner cover layer. The core and/or the cover layers may be formed of more than one layer and an intermediate or mantle layer may be disposed between the core and the cover of the golf ball. The innermost portion of the core, while preferably solid, may be a hollow or a liquid-, gel-, or air-filled sphere. As with the core, the cover layers may also comprise a plurality of layers. The core may also comprise a solid or liquid filled center around which many yards of a tensioned elastomeric material are wound.

The materials for solid cores include compositions having a base rubber, a crosslinking agent, a filler, a halogenated organosulfur compound, and a co-crosslinking or initiator agent. The base rubber typically includes natural or synthetic rubbers. A preferred base rubber is 1,4-polybutadiene having a cis-structure of at least 40%, more preferably at least about 90%, and most preferably at least about 95%. Most preferably, the base rubber comprises high-Mooney-viscosity rubber. Preferably, the base rubber has a Mooney

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viscosity greater than about 35, more preferably greater than about 50. Preferably, the polybutadiene rubber has a molecular weight greater than about 400,000 and a polydispersity of no greater than about 2. Examples of desirable polybutadiene rubbers include BUNA® CB22 and BUNA® CB23, commercially available from Bayer of Akron, Ohio; UBE-POL® 360 L and UBEPOL® 150L, commercially available from UBE Industries of Tokyo, Japan; and CARIFLEX® BCP820 and CARIFLEX® BCP824, commercially available from Shell of Houston, Tex. If desired, the polybutadiene can also be mixed with other elastomers known in the art such as natural rubber, polyisoprene rubber and/or styrene-butadiene rubber in order to modify the properties of the core.

The crosslinking agent includes a metal salt, such as a zinc salt or a magnesium unsaturated fatty acid, such as acrylic or methacrylic acid, having 3 to 8 carbon atoms. Examples include, but are not limited to, one or more metal salt diacrylates, dimethacrylates, and monomethacrylates, wherein the metal is magnesium, calcium, zinc, aluminum, sodium, lithium, or nickel. Preferred acrylates include zinc acrylate, zinc diacrylate, zinc methacrylate, zinc dimethacrylate, and mixtures thereof. The crosslinking agent is typically present in an amount greater than about 10 parts per hundred ("pph") parts of the base polymer, preferably from about 20 to 40 pph of the base polymer, more preferably from about 25 to 35 pph of the base polymer.

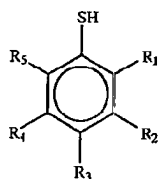
The initiator agent can be any known polymerization initiator which decomposes during the cure cycle. Suitable initiators include organic peroxide compounds, such as dicumyl peroxide; 1,1-di-(t-butylperoxy) 3,3,5-trimethyl cyclohexane;  $\alpha,\alpha$ -bis (t-butylperoxy) diisopropylbenzene; 2,5-dimethyl-2,5 di(t-butylperoxy) hexane; di-t-butyl peroxide; and mixtures thereof. Other examples include, but are not limited to, VAROX® 231XL and VAROX® DCP-R, commercially available from Elf Atochem of Philadelphia, Pa.; PERKODOX® BC and PERKODOX® 14, commercially available from Akzo Nobel of Chicago, Ill.; and ELASTOCHEM® DCP-70, commercially available from Rhein Chemie of Trenton, N.J.

It is well known that peroxides are available in a variety of forms having different activity. The activity is typically defined by the "active oxygen content." For example, PERKODOX® BC peroxide is 98% active and has an active oxygen content of 5.80%, whereas PERKODOX® DCP-70 is 70% active and has an active oxygen content of 4.18%. If the peroxide is present in pure form, it is preferably present in an amount of at least about 0.25 pph, more preferably between about 0.35 pph and about 2.5 pph, and most preferably between about 0.5 pph and about 2 pph. Peroxides are also available in concentrate form, which are well-known to have differing activities, as described above. In this case, if concentrate peroxides are employed in the present invention, one skilled in the art would know that the concentrations suitable for pure peroxides are easily adjusted for concentrate peroxides by dividing by the activity. For example, 2 pph of a pure peroxide is equivalent 4 pph of a concentrate peroxide that is 50% active (i.e., 2 divided by 0.5=4).

The halogenated organosulfur compounds of the present invention include, but are not limited to those having the following general formula:

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where  $R_1$ - $R_5$  can be  $C_1$ - $C_8$  alkyl groups; halogen groups; thiol groups ( $-SH$ ), carboxylated groups; sulfonated groups; and hydrogen; in any order; and also pentafluorothiophenol; 2-fluorothiophenol; 3-fluorothiophenol; 4-fluorothiophenol; 2,3-fluorothiophenol; 2,4-fluorothiophenol; 3,4-fluorothiophenol; 3,5-fluorothiophenol; 2,3,4-fluorothiophenol; 3,4,5-fluorothiophenol; 2,3,4,5-tetrafluorothiophenol; 2,3,5,6-tetrafluorothiophenol; 4-chlorotetrafluorothiophenol; pentachlorothiophenol; 2-chlorothiophenol; 3-chlorothiophenol; 4-chlorothiophenol; 2,3-chlorothiophenol; 2,4-chlorothiophenol; 3,4-chlorothiophenol; 3,5-chlorothiophenol; 2,3,4-chlorothiophenol; 3,4,5-chlorothiophenol; 2,3,4,5-tetrachlorothiophenol; 2,3,5,6-tetrachlorothiophenol; pentabromothiophenol; 2-bromothiophenol; 3-bromothiophenol; 4-bromothiophenol; 2,3-bromothiophenol; 2,4-bromothiophenol; 3,4-bromothiophenol; 3,5-bromothiophenol; 2,3,4-bromothiophenol; 3,4,5-bromothiophenol; 2,3,4,5-tetrabromothiophenol; 2,3,5,6-tetrabromothiophenol; pentaiodothiophenol; 2-iodothiophenol; 3-iodothiophenol; 4-iodothiophenol; 2,3-iodothiophenol; 2,4-iodothiophenol; 3,4-iodothiophenol; 3,5-iodothiophenol; 2,3,4-iodothiophenol; 3,4,5-iodothiophenol; 2,3,4,5-tetraiodothiophenol; 2,3,5,6-tetraiodothiophenol; and their zinc salts. Preferably, the halogenated organosulfur compound is pentachlorothiophenol, which is commercially available in neat form or under the tradename STRUKTOL®, a clay-based carrier containing the sulfur compound pentachlorothiophenol loaded at 45 percent (correlating to 2.4 parts PCTP). STRUKTOL® is commercially available from Struktol Company of America of Stow, Ohio. PCTP is commercially available in neat or salt form from cChinacem of San Francisco, Calif. Most preferably, the halogenated organosulfur compound is the zinc salt of pentachlorothiophenol. The halogenated organosulfur compounds of the present invention are preferably present in an amount greater than about 2.2 pph, more preferably between about 2.3 pph and about 5 pph, and most preferably between about 2.3 and about 4 pph.

Fillers typically include materials such as tungsten, zinc oxide, barium sulfate, silica, calcium carbonate, zinc carbonate, metals, metal oxides and salts, regrind (recycled core material typically ground to about 30 mesh particle), high-Mooney-viscosity rubber regrind, UV absorbers, hindered amine light stabilizers, optical brighteners, and the like. Fillers added to one or more portions of the golf ball typically include processing aids or compounds to affect Theological and mixing properties, density-modifying fillers, tear strength, or reinforcement fillers, and the like. The fillers are generally inorganic, and suitable fillers include numerous metals or metal oxides, such as zinc oxide and tin oxide, as well as barium sulfate, zinc sulfate, calcium carbonate, barium carbonate, clay, tungsten, tungsten carbide, an array of silicas, and mixtures thereof. Fillers may also include various foaming agents or blowing agents which may be readily selected by one of ordinary skill in the

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art. Fillers may include polymeric, ceramic, metal, and glass microspheres may be solid or hollow, and filled or unfilled. Fillers are typically also added to one or more portions of the golf ball to modify the density thereof to conform to uniform golf ball standards. Fillers may also be used to modify the weight of the center or at least one additional layer for specialty balls.

The invention also includes a method to convert the cis-isomer of the polybutadiene resilient polymer component to the trans-isomer during a molding cycle and to form a golf ball. A variety of methods and materials suitable for cis-to-trans conversion have been disclosed in U.S. Pat. No. 6,162,135 and U.S. application Ser. No. 09/461,736, filed Dec. 16, 1999; Ser. No. 09/458,676, filed Dec. 10, 1999; and Ser. No. 09/461,421, filed Dec. 16, 1999, each of which are incorporated herein, in their entirety, by reference.

The materials used in forming either the golf ball center or any portion of the core, in accordance with the invention, may be combined to form a mixture by any type of mixing known to one of ordinary skill in the art. Suitable types of mixing include single pass and multi-pass mixing. Suitable mixing equipment is well known to those of ordinary skill in the art, and such equipment may include a Banbury mixer, a two-roll mill, or a twin screw extruder.

Conventional mixing speeds for combining polymers are typically used. The mixing temperature depends upon the type of polymer components, and more importantly, on the type of free-radical initiator. Suitable mixing speeds and temperatures are well-known to those of ordinary skill in the art, or may be readily determined without undue experimentation.

The mixture can be subjected to, e.g., a compression or injection molding process, to obtain solid spheres for the center or hemispherical shells for forming an intermediate layer. The temperature and duration of the molding cycle are selected based upon reactivity of the mixture. The molding cycle may have a single step of molding the mixture at a single temperature for a fixed time duration. The molding cycle may also include a two-step process, in which the polymer mixture is held in the mold at an initial temperature for an initial duration of time, followed by holding at a second, typically higher temperature for a second duration of time. In a preferred embodiment of the current invention, a single-step cure cycle is employed. The materials used in forming either the golf ball center or any portion of the core, in accordance with the invention, may be combined to form a golf ball by an injection molding process, which is also well-known to one of ordinary skill in the art. Although the curing time depends on the various materials selected, those of ordinary skill in the art will be readily able to adjust the curing time upward or downward based on the particular materials used and the discussion herein.

Properties that are desirable for the cover include good moldability, high abrasion resistance, high tear strength, high resilience, and good mold release. The cover typically has a thickness to provide sufficient strength, good performance characteristics, and durability. The cover preferably has a thickness of less than about 0.1 inches, more preferably, less than about 0.05 inches, and most preferably, between about 0.02 inches and about 0.04 inches. The invention is particularly directed towards a multilayer golf ball which comprises a core, an inner cover layer, and an outer cover layer. In this embodiment, preferably, at least one of the inner and outer cover layer has a thickness of less than about 0.05 inches, more preferably between about 0.02 inches and about 0.04 inches. Most preferably, the thickness of either layer is about 0.03 inches.

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When the golf ball of the present invention includes an inner cover layer, this layer can include any materials known to those of ordinary skill in the art, including thermoplastic and thermosetting material, but preferably the inner cover can include any suitable materials, such as ionic copolymers of ethylene and an unsaturated monocarboxylic acid which are available under the trademark SURLYN® of E. I. DuPont de Nemours & Co., of Wilmington, Del., or IOTEK® or ESCOR® of Exxon. These are copolymers or terpolymers of ethylene and methacrylic acid or acrylic acid partially neutralized with salts of zinc, sodium, lithium, magnesium, potassium, calcium, manganese, nickel or the like, in which the salts are the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially neutralized and might include methacrylic, crotonic, maleic, fumaric or itaconic acid.

This golf ball can likewise include one or more homopolymeric or copolymeric inner cover materials, such as:

(1) Vinyl resins, such as those formed by the polymerization of vinyl chloride, or by the copolymerization of vinyl chloride with vinyl acetate, acrylic esters or vinylidene chloride;

(2) Polyolefins, such as polyethylene, polypropylene, polybutylene and copolymers such as ethylene methylacrylate, ethylene ethylacrylate, ethylene vinyl acetate, ethylene methacrylic or ethylene acrylic acid or propylene acrylic acid and copolymers and homopolymers produced using a single-site catalyst or a metallocene catalyst;

(3) Polyurethanes, such as those prepared from polyols and diisocyanates or polyisocyanates and those disclosed in U.S. Pat. No. 5,334,673;

(4) Polyureas, such as those disclosed in U.S. Pat. No. 5,484,870;

(5) Polyamides, such as poly(hexamethylene adipamide) and others prepared from diamines and dibasic acids, as well as those from amino acids such as poly(caprolactam), and blends of polyamides with SURLYN®, polyethylene, ethylene copolymers, ethyl-propylene-non-conjugated diene terpolymer, and the like;

(6) Acrylic resins and blends of these resins with poly vinyl chloride, elastomers, and the like;

(7) Thermoplastics, such as urethanes; olefinic thermoplastic rubbers, such as blends of polyolefins with ethylene-propylene-non-conjugated diene terpolymer; block copolymers of styrene and butadiene, isoprene or ethylene-butylene rubber; or copoly(ether-amide), such as PEBAX®, sold by ELF Atochem of Philadelphia, Pa.;

(8) Polyphenylene oxide resins or blends of polyphenylene oxide with high impact polystyrene as sold under the trademark NORYL® by General Electric Company of Pittsfield, Mass.;

(9) Thermoplastic polyesters, such as polyethylene terephthalate, polybutylene terephthalate, polyethylene terephthalate/glycol modified and elastomers sold under the trademarks HYTREL® by E. I. DuPont de Nemours & Co. of Wilmington, Del., and LOMOD® by General Electric Company of Pittsfield, Mass.;

(10) Blends and alloys, including polycarbonate with acrylonitrile butadiene styrene, polybutylene terephthalate, polyethylene terephthalate, styrene maleic anhydride, polyethylene, elastomers, and the like, and polyvinyl chloride with acrylonitrile butadiene styrene or ethylene vinyl acetate or other elastomers; and

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(11) Blends of thermoplastic rubbers with polyethylene, propylene, polyacetal, nylon, polyesters, cellulose esters, and the like.

Preferably, the inner cover includes polymers, such as ethylene, propylene, butene-1 or hexane-1 based homopolymers or copolymers including functional monomers, such as acrylic and methacrylic acid and fully or partially neutralized ionomer resins and their blends, methyl acrylate, methyl methacrylate homopolymers and copolymers, imidized, amino group containing polymers, polycarbonate, reinforced polyamides, polyphenylene oxide, high impact polystyrene, polyether ketone, polysulfone, poly(phenylene sulfide), acrylonitrile-butadiene, acrylic-styrene-acrylonitrile, poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene vinyl alcohol), poly(tetrafluoroethylene) and their copolymers including functional comonomers, and blends thereof. Suitable cover compositions also include a polyether or polyester thermoplastic urethane, a thermoset polyurethane, a low modulus ionomer, such as acid-containing ethylene copolymer ionomers, including E/X/Y terpolymers where E is ethylene, X is an acrylate or methacrylate-based softening comonomer present in about 0 to 50 weight percent and Y is acrylic or methacrylic acid present in about 5 to 35 weight percent. Preferably, the acrylic or methacrylic acid is present in about 8 to 35 weight percent, more preferably 8 to 25 weight percent, and most preferably 8 to 20 weight percent.

Any of the inner or outer cover layers may also be formed from polymers containing  $\alpha$ ,  $\beta$ -unsaturated carboxylic acid groups, or the salts thereof, that have been 100 percent neutralized by organic fatty acids. The acid moieties of the highly-neutralized polymers ("HNP"), typically ethylene-based ionomers, are preferably neutralized greater than about 70%, more preferably greater than about 90%, and most preferably at least about 100%. The HNP's can be also be blended with a second polymer component, which, if containing an acid group, may be neutralized in a conventional manner, by the organic fatty acids of the present invention, or both. The second polymer component, which may be partially or fully neutralized, preferably comprises ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, polyamides, polycarbonates, polyesters, polyurethanes, polyureas, thermoplastic elastomers, polybutadiene rubber, balata, metallocene-catalyzed polymers (grafted and non-grafted), single-site polymers, high-crystalline acid polymers, cationic ionomers, and the like.

The acid copolymers can be described as E/X/Y copolymers where E is ethylene, X is an  $\alpha$ ,  $\beta$ -ethylenically unsaturated carboxylic acid, and Y is a softening comonomer. In a preferred embodiment, X is acrylic or methacrylic acid and Y is a C<sub>1-8</sub> alkyl acrylate or methacrylate ester. X is preferably present in an amount from about 1 to about 35 weight percent of the polymer, more preferably from about 5 to about 30 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer. Y is preferably present in an amount from about 0 to about 50 weight percent of the polymer, more preferably from about 5 to about 25 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer.

The organic acids are aliphatic, mono-functional (saturated, unsaturated, or multi-unsaturated) organic acids. Salts of these organic acids may also be employed. The salts of organic acids of the present invention include the salts of barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, or

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calcium, salts of fatty acids, particularly stearic, bebenic, erucic, oleic, linoleic or dimerized derivatives thereof. It is preferred that the organic acids and salts of the present invention be relatively non-migratory (they do not bloom to the surface of the polymer under ambient temperatures) and non-volatile (they do not volatilize at temperatures required for melt-blending).

Thermoplastic polymer components, such as copolyetheresters, copolyesteresters, copolyetheramides, elastomeric polyolefins, styrene diene block copolymers and their hydrogenated derivatives, copolyesteramides, thermoplastic polyurethanes, such as copolyetherurethanes, copolyesterurethanes, copolyureaurethanes, epoxy-based polyurethanes, polycaprolactone-based polyurethanes, polyureas, and polycarbonate-based polyurethanes fillers, and other ingredients, if included, can be blended in either before, during, or after the acid moieties are neutralized, thermoplastic polyurethanes.

Examples of these materials are disclosed in U.S. Patent Application Publication Nos. 2001/0018375 and 2001/0019971, which are incorporated herein in their entirety by express reference thereto.

While the outer cover may be formed of any of the above-listed materials, the outer cover preferably includes a polyurethane, polyurea, or epoxy composition, generally comprising the reaction product of at least one polyisocyanate, polyol, and at least one curing agent. Any polyisocyanate available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyisocyanates include, but are not limited to, 4,4'-diphenylmethane diisocyanate ("MDI"); polymeric MDI; carbodiimide-modified liquid MDI; 4,4'-dicyclohexylmethane diisocyanate ("H<sub>12</sub>MDI"); p-phenylene diisocyanate ("PPDI"); m-phenylene diisocyanate ("MPDI"); toluene diisocyanate ("TDI"); 3,3'-dimethyl-4,4'-biphenylene diisocyanate ("TODI"); isophoronediiisocyanate ("IPDI"); hexamethylene diisocyanate ("HDI"); naphthalene diisocyanate ("NDI"); xylene diisocyanate ("XDI"); p-tetramethylxylene diisocyanate ("p-TMXDI"); m-tetramethylxylene diisocyanate ("m-TMXDI"); ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; cyclohexyl diisocyanate; 1,6-hexamethylene-diisocyanate ("HDI"); dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,4,4-trimethyl-1,6-hexane diisocyanate ("TMDI"); tetracene diisocyanate; naphthalene diisocyanate; anthracene diisocyanate; isocyanurate of toluene diisocyanate; uretdione of hexamethylene diisocyanate; and mixtures thereof. Preferably, the polyisocyanate includes MDI, PPDI, TDI, or a mixture thereof, and more preferably, the polyisocyanate includes MDI. It should be understood that, as used herein, the term "MDI" includes 4,4'-diphenylmethane diisocyanate, polymeric MDI, carbodiimide-modified liquid MDI, and mixtures thereof and, additionally, that the diisocyanate employed may be "low free monomer," understood by one of ordinary skill in the art to have lower levels of "free" monomer isocyanate groups, typically less than about 0.1% free monomer groups. Examples of "low free monomer" diisocyanates include, but are not limited to Low Free Monomer MDI, Low Free Monomer TDI, and Low Free Monomer PPDI.

The at least one polyisocyanate should have less than about 14% unreacted NCO groups. Preferably, the at least

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one polyisocyanate has no greater than about 7.5% NCO, and more preferably, less than about 7.0%. It is well understood in the art that the hardness of polyurethane can be correlated to the percent of unreacted NCO groups (See FIG. 1) As such, if the polyisocyanate has less than about 7.0% unreacted groups, the corresponding polyurethane material will have a material hardness of less than about 50 Shore D.

It should be understood, especially to one of ordinary skill in the art, that there is a fundamental difference between "material hardness" and "hardness, as measured directly on a golf ball." Material hardness is defined by the procedure set forth in ASTM-D2240 and generally involves measuring the hardness of a flat "slab" or "button" formed of the material of which the hardness is to be measured. Hardness, when measured directly on a golf ball (or other spherical surface) is a completely different measurement and, therefore, results in a different hardness value. This difference results from a number of factors including, but not limited to, ball construction (i.e., core type, number of core and/or cover layers, etc.), ball (or sphere) diameter, and the material composition of adjacent layers. It should also be understood that the two measurement techniques are not linearly related and, therefore, one hardness value cannot easily be correlated to the other.

Any polyol available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyols include, but are not limited to, polyether polyols, hydroxy-terminated polybutadiene (including partially/fully hydrogenated derivatives), polyester polyols, polycaprolactone polyols, and polycarbonate polyols. In one preferred embodiment, the polyol includes polyether polyol. Examples include, but are not limited to, polytetramethylene ether glycol ("PTMEG"), polyethylene propylene glycol, polyoxypropylene glycol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds and substituted or unsubstituted aromatic and cyclic groups. Preferably, the polyol of the present invention includes PTMEG.

Suitable polyester polyols include, but are not limited to, polyethylene adipate glycol; polybutylene adipate glycol; polyethylene propylene adipate glycol; o-phthalate-1,6-hexanediol; poly(hexamethylene adipate) glycol; and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

Suitable polycaprolactone polyols include, but are not limited to, 1,6-hexanediol-initiated polycaprolactone, diethylene glycol initiated polycaprolactone, trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, PTMEG-initiated polycaprolactone, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

Suitable polycarbonates include, but are not limited to, polyphthalate carbonate and poly(hexamethylene carbonate) glycol. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

Polyamine curatives are also suitable for use in polyurethane covers. Preferred polyamine curatives include, but are not limited to, 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, 3,5-diethyltoluene-2,4-diamine and isomers thereof, such as 3,5-diethyltoluene-2,6-diamine; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline)

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("MCDEA"); polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkyldiamino diphenyl methane; p,p'-methylene dianiline ("MDA"); m-phenylenediamine ("MPDA"); 4,4'-methylene-bis-(2-chloroaniline) ("MOCA"); 4,4'-methylene-bis-(2,6-diethylaniline) ("MDEA"); 4,4'-methylene-bis-(2,3-dichloroaniline) ("MDCA"); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenylmethane; trimethylene glycol di-p-aminobenzoate; and mixtures thereof. Preferably, the curing agent of the present invention includes 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, such as Ethacure® 300, commercially available from Albermarle Corporation of Baton Rouge, La. Suitable polyamine curatives include both primary and secondary amines.

At least one of a diol, triol, tetraol, or hydroxy-terminated curatives may be added to the aforementioned polyurethane composition. Suitable diol, triol, and tetraol groups include ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis-(2-hydroxyethoxy) benzene; 1,3-bis-[2-(2-hydroxyethoxy) ethoxy] benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy) ethoxy] ethoxy] benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(β-hydroxyethyl) ether; hydroquinone-di-(β-hydroxyethyl) ether; and mixtures thereof. Preferred hydroxy-terminated curatives include 1,3-bis(2-hydroxyethoxy) benzene; 1,3-bis-[2-(2-hydroxyethoxy) ethoxy] benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy) ethoxy] ethoxy] benzene; 1,4-butanediol, and mixtures thereof.

Both the hydroxy-terminated and amine curatives can include one or more saturated, unsaturated, aromatic, and cyclic groups. Additionally, the hydroxy-terminated and amine curatives can include one or more halogen groups. The polyurethane composition can be formed with a blend or mixture of curing agents. If desired, however, the polyurethane composition may be formed with a single curing agent.

In a particularly preferred embodiment of the present invention, saturated polyurethanes used to form cover layers, preferably the outer cover layer, and may be selected from among both castable thermoset and thermoplastic polyurethanes. In this embodiment, the saturated polyurethanes are substantially free of aromatic groups or moieties.

Saturated diisocyanates which can be used include, but are not limited to, ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene-diisocyanate; 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; dicyclohexylmethane diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isophorone diisocyanate ("IPDI"); methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate ("TMDI"). The most preferred saturated diisocyanates are 4,4'-dicyclohexylmethane diisocyanate and isophorone diisocyanate ("IPDI").

Saturated polyols which are appropriate for use in this invention include, but are not limited to, polyether polyols such as polytetramethylene ether glycol and poly(oxypropylene) glycol. Suitable saturated polyester polyols include polyethylene adipate glycol, polyethylene propylene adipate glycol, polybutylene adipate glycol, polycarbonate polyol and ethylene oxide-capped polyoxypropylene diols. Saturated polycaprolactone polyols which are useful in the

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invention include diethylene glycol initiated polycaprolactone, 1,4-butanediol initiated polycaprolactone, 1,6-hexanediol initiated polycaprolactone; trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, PTMEG-initiated polycaprolactone. The most preferred saturated polyols are PTMEG and PTMEG-initiated polycaprolactone.

Suitable saturated curatives include 1,4-butanediol, ethylene glycol, diethylene glycol, polytetramethylene ether glycol, propylene glycol; trimethanolpropane; tetra-(2-hydroxypropyl)-ethylenediamine; isomers and mixtures of isomers of cyclohexyldimethylol, isomers and mixtures of isomers of cyclohexane bis(methylamine); triisopropanolamine, ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, 4,4'-dicyclohexylmethane diamine, 2,2,4-trimethyl-1,6-hexanediol; 2,4,4-trimethyl-1,6-hexanediol; diethyleneglycol di-(aminopropyl)ether; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,2-bis-(sec-butylamino)cyclohexane; 1,4-bis-(sec-butylamino)cyclohexane; isophorone diamine, hexamethylene diamine, propylene diamine, 1-methyl-2,4-cyclohexyl diamine, 1-methyl-2,6-cyclohexyl diamine, 1,3-diaminopropane, dimethylamino propylamine, diethylamino propylamine, imido-bis-propylamine, isomers and mixtures of isomers of diaminocyclohexane, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, and diisopropanolamine. The most preferred saturated curatives are 1,4-butanediol, 1,4-cyclohexyldimethylol and 4,4'-bis-(sec-butylamino)-dicyclohexylmethane.

Suitable catalysts include, but are not limited to bismuth catalyst, oleic acid, triethylenediamine (DABCO®-33LV), di-butyltin dilaurate (DABCO®-T12) and acetic acid. The most preferred catalyst is di-butyltin dilaurate (DABCO®-T12). DABCO® materials are manufactured by Air Products and Chemicals, Inc.

It is well known in the art that if the saturated polyurethane materials are to be blended with other thermoplastics, care must be taken in the formulation process so as to produce an end product which is thermoplastic in nature. Thermoplastic materials may be blended with other thermoplastic materials, but thermosetting materials are difficult if not impossible to blend homogeneously after the thermosetting materials are formed. Preferably, the saturated polyurethane comprises from about 1 to about 100%, more preferably from about 10 to about 75% of the cover composition and/or the intermediate layer composition. About 90 to about 10%, more preferably from about 90 to about 25% of the cover and/or the intermediate layer composition is comprised of one or more other polymers and/or other materials as described below. Such polymers include, but are not limited to polyurethane/polyurea ionomers, polyurethanes or polyureas, epoxy resins, polyethylenes, polyamides and polyesters, polycarbonates and polyacrylin. Unless otherwise stated herein, all percentages are given in percent by weight of the total composition of the golf ball layer in question.

Polyurethane prepolymers are produced by combining at least one polyol, such as a polyether, polycaprolactone, polycarbonate or a polyester, and at least one isocyanate. Thermosetting polyurethanes are obtained by curing at least one polyurethane prepolymer with a curing agent selected from a polyamine, triol or tetraol. Thermoplastic polyurethanes are obtained by curing at least one polyurethane prepolymer with a diol curing agent. The choice of the curatives is critical because some urethane elastomers that are cured with a diol and/or blends of diols do not produce

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urethane elastomers with the impact resistance required in a golf ball cover. Blending the polyamine curatives with diol cured urethane elastomeric formulations leads to the production of thermoset urethanes with improved impact and cut resistance.

Thermoplastic polyurethanes may be blended with suitable materials to produce a thermoplastic end product. Examples of such additional materials may include ionomers such as the SURLYN®, ESCOR® and IOTEK® copolymers described above.

Other suitable materials which may be combined with the saturated polyurethanes in forming the cover and/or intermediate layer(s) of the golf balls of the invention include ionic or non-ionic polyurethanes and polyureas, epoxy resins, polyethylenes, polyamides and polyesters. For example, the cover and/or intermediate layer may be formed from a blend of at least one saturated polyurethane and thermoplastic or thermoset ionic and non-ionic urethanes and polyurethanes, cationic urethane ionomers and urethane epoxies, ionic and non-ionic polyureas and blends thereof. Examples of suitable urethane ionomers are disclosed in U.S. Pat. No. 5,692,974, the disclosure of which is hereby incorporated by reference in its entirety. Other examples of suitable polyurethanes are described in U.S. Pat. No. 5,334,673. Examples of appropriate polyureas are discussed in U.S. Pat. No. 5,484,870 and examples of suitable polyurethanes cured with epoxy group containing curing agents are disclosed in U.S. Pat. No. 5,908,358, the disclosures of which are hereby incorporated herein by reference in their entirety.

A variety of conventional components can be added to the cover compositions of the present invention. These include, but are not limited to, white pigment such as TiO<sub>2</sub>, ZnO, optical brighteners, surfactants, processing aids, foaming agents, density-controlling fillers, UV stabilizers and light stabilizers. Saturated polyurethanes are resistant to discoloration. However, they are not immune to deterioration in their mechanical properties upon weathering. Addition of UV absorbers and light stabilizers to any of the above compositions and, in particular, the polyurethane compositions, help to maintain the tensile strength, elongation, and color stability. Suitable UV absorbers and light stabilizers include TINUVIN® 328, TINUVIN® 213, TINUVIN® 765, TINUVIN® 770 and TINUVIN® 622. The preferred UV absorber is TINUVIN® 328, and the preferred light stabilizer is TINUVIN® 765. TINUVIN® products are available from Ciba-Geigy. Dyes, as well as optical brighteners and fluorescent pigments may also be included in the golf ball covers produced with polymers formed according to the present invention. Such additional ingredients may be added in any amounts that will achieve their desired purpose.

Any method known to one of ordinary skill in the art may be used to polyurethanes of the present invention. One commonly employed method, known in the art as a one-shot method, involves concurrent mixing of the polyisocyanate, polyol, and curing agent. This method results in a mixture that is inhomogeneous (more random) and affords the manufacturer less control over the molecular structure of the resultant composition. A preferred method of mixing is known as a prepolymer method. In this method, the polyisocyanate and the polyol are mixed separately prior to addition of the curing agent. This method affords a more homogeneous mixture resulting in a more consistent polymer composition. Other methods suitable for forming the layers of the present invention include reaction injection molding ("RIM"), liquid injection molding ("LIM"), and

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pre-reacting the components to form an injection moldable thermoplastic polyurethane and then injection molding, all of which are known to one of ordinary skill in the art.

It has been found by the present invention that the use of a castable, reactive material, which is applied in a fluid form, makes it possible to obtain very thin outer cover layers on golf balls. Specifically, it has been found that castable, reactive liquids, which react to form a urethane elastomer material, provide desirable very thin outer cover layers.

The castable, reactive liquid employed to form the urethane elastomer material can be applied over the core using a variety of application techniques such as spraying, dipping, spin coating, or flow coating methods which are well known in the art. An example of a suitable coating technique is that which is disclosed in U.S. Pat. No. 5,733,428, the disclosure of which is hereby incorporated by reference in its entirety in the present application.

The outer cover is preferably formed around the inner cover by mixing and introducing the material in the mold halves. It is important that the viscosity be measured over time, so that the subsequent steps of filling each mold half, introducing the core into one half and closing the mold can be properly timed for accomplishing centering of the core cover halves fusion and achieving overall uniformity. Suitable viscosity range of the curing urethane mix for introducing cores into the mold halves is determined to be approximately between about 2,000 cP and about 30,000 cP, with the preferred range of about 8,000 cP to about 15,000 cP.

To start the cover formation, mixing of the prepolymer and curative is accomplished in motorized mixer including mixing head by feeding through lines metered amounts of curative and prepolymer. Top preheated mold halves are filled and placed in fixture units using centering pins moving into holes in each mold. At a later time, a bottom mold half or a series of bottom mold halves have similar mixture amounts introduced into the cavity. After the reacting materials have resided in top mold halves for about 40 to about 80 seconds, a core is lowered at a controlled speed into the gelling reacting mixture.

A ball cup holds the ball core through reduced pressure (or partial vacuum). Upon location of the coated core in the halves of the mold after gelling for about 40 to about 80 seconds, the vacuum is released allowing core to be released. The mold halves, with core and solidified cover half thereon, are removed from the centering fixture unit, inverted and mated with other mold halves which, at an appropriate time earlier, have had a selected quantity of reacting polyurethane prepolymer and curing agent introduced therein to commence gelling.

Similarly, U.S. Pat. No. 5,006,297 and U.S. Pat. No. 5,334,673 both also disclose suitable molding techniques which may be utilized to apply the castable reactive liquids employed in the present invention. Further, U.S. Pat. Nos. 6,180,040 and 6,180,722 disclose methods of preparing dual core golf balls. The disclosures of these patents are hereby incorporated by reference in their entirety. However, the method of the invention is not limited to the use of these techniques.

In one embodiment of the golf ball of the present invention, the center has a first hardness, the outer core layer has a second hardness greater than the first, and the inner cover layer has a third hardness greater than the second. Additionally, it is preferred that the outer cover layer has a fourth hardness less than the third hardness.

The molding process and composition of golf ball portions typically results in a gradient of material properties.

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Methods employed in the prior art generally exploit hardness to quantify these gradients. Hardness is a qualitative measure of static modulus and does not represent the modulus of the material at the deformation rates associated with golf ball use, i.e., impact by a club. As is well known to one skilled in the art of polymer science, the time-temperature superposition principle may be used to emulate alternative deformation rates. For golf ball portions including polybutadiene, a 1-Hz oscillation at temperatures between 0° C. and -50° C. are believed to be qualitatively equivalent to golf ball impact rates. Therefore, measurement of loss tangent and dynamic stiffness at 0° C. to -50° C. may be used to accurately anticipate golf ball performance, preferably at temperatures between about -20° C. and -50° C.

The resultant golf balls typically have a coefficient of restitution of greater than about 0.7, preferably greater than about 0.75, and more preferably greater than about 0.78. The golf balls also typically have an Atti compression of at least about 40, preferably from about 50 to 120, and more preferably from about 60 to 100. The golf ball cured polybutadiene material typically has a hardness of at least about 15 Shore A, preferably between about 30 Shore A and 80 Shore D, more preferably between about 50 Shore A and 60 Shore D.

When golf balls are prepared according to the invention, they typically will have dimple coverage greater than about 60 percent, preferably greater than about 65 percent, and more preferably greater than about 75 percent. The flexural modulus of the cover on the golf balls, as measured by ASTM method D6272-98, Procedure B, is typically greater than about 500 psi, and is preferably from about 500 psi to 150,000 psi. As discussed herein, the outer cover layer is preferably formed from a relatively soft polyurethane material. In particular, the material of the outer cover layer should have a material hardness, as measured by ASTM-D2240, less than about 60 Shore D, more preferably between about 25 and about 50 Shore D, and most preferably between about 45 and about 48 Shore D. The inner cover layer preferably has a material hardness of less than about 70 Shore D, more preferably between about 30 and about 70 Shore D, and most preferably, between about 50 and about 65 Shore D.

The core of the present invention has a Soft Center Deflection Index ("SCDI") compression of less than about 160, more preferably, between about 40 and about 160, and most preferably, between about 60 and about 120. In an alternative, low compression embodiment, the core has an Atti compression less than about 20, more preferably less than about 10, and most preferably, 0.

The SCDI is a program change for the Dynamic Compression Machine ("DCM") that allows determination of the pounds required to deflect a core 10% of its diameter. The DCM is an apparatus that applies a load to a core or ball and measures the number of inches the core or ball is deflected at measured loads. A crude load/deflection curve is gener-

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ated that is fit to the Atti compression scale that results in a number being generated that represents an Atti compression. The DCM does this via a load cell attached to the bottom of a hydraulic cylinder that is triggered pneumatically at a fixed rate (typically about 1.0 ft/s) towards a stationary core. Attached to the cylinder is an LVDT that measures the distance the cylinder travels during the testing timeframe. A software-based logarithmic algorithm ensures that measurements are not taken until at least five successive increases in load are detected during the initial phase of the test.

The SCDI is a slight variation of this set up. The hardware is the same, but the software and output has changed. With the SCDI, we are only interested in the pounds of force required to deflect a core x amount of inches. That amount of deflection is 10% percent of the core's diameter. The DCM is triggered, the cylinder deflects the core by 10% of its diameter, and the DCM reports back the pounds of force required (as measured from the attached load cell) to deflect the core by that amount. The value displayed is a single number in units of pounds.

The overall outer diameter ("OD") of the core is less than about 1.610 inches, preferably, no greater than 1.590 inches, more preferably between about 1.540 inches and about 1.580 inches, and most preferably between about 1.50 inches to about 1.570 inches. The OD of the inner cover layer is preferably between 1.580 inches and about 1.640 inches, more preferably between about 1.590 inches to about 1.630 inches, and most preferably between about 1.600 inches to about 1.630 inches.

The present multilayer golf ball can have an overall diameter of any size. Although the United States Golf Association ("USGA") specifications limit the minimum size of a competition golf ball to 1.680 inches. There is no specification as to the maximum diameter. Golf balls of any size, however, can be used for recreational play. The preferred diameter of the present golf balls is from about 1.680 inches to about 1.800 inches. The more preferred diameter is from about 1.680 inches to about 1.760 inches. The most preferred diameter is about 1.680 inches to about 1.740 inches.

#### EXAMPLE

Three solid cores, each having an outer diameter of 1.58 inches, were formed of a composition comprising polybutadiene rubber, zinc diacrylate, zinc oxide, dicumyl peroxide, barium sulfate, and color dispersion. One core, representative of conventional technology, was used as a control. The two remaining cores were each additionally blended with 5.3 parts Struktol® (Example 1) and the zinc salt of pentachlorothiophenol at 2.4 parts (Example 2). Struktol® at 5.3 parts contains 2.4 parts PCTP. The specific compositions for each of the solid cores are presented below in Table I.

TABLE I

	CONTROL				EXAMPLE 1				EXAMPLE 2			
INGREDIENT												
polybutadiene rubber	100	100	100	100	100	100	100	100	100	100	100	100
zinc diacrylate	18	25	30	27	34	41	20	25	30	35		
dicumyl peroxide	0.5	0.5	0.5	1.8	1.8	1.8	0.8	0.8	0.8	0.8		
Struktol® A95	—	—	—	5.3	5.3	5.3	—	—	—	—		
zinc salt of PCTP	—	—	—	—	—	—	2.4	2.4	2.4	2.4		
zinc oxide	26.5	24.1	22.2	5	5	.5	5	5	5	5		

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TABLE I-continued

	CONTROL				EXAMPLE 1			EXAMPLE 2		
barium sulfate	—	—	—	16.2	13.4	10.6	21.7	19.7	17.7	15.7
color dispersion	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14
PROPERTY										
Effective Modulus (psi)	3800	6200	8700	4100	6200	7700	3600	5100	7400	9700
Atti Compression	17	52	76	22	52	67	13	38	65	84
COR @ 125 ft/s	0.764	0.789	0.802	0.773	0.7941	0.802	0.782	0.801	0.813	0.823

It is very apparent that the addition of PCTP, in either form, increases COR, decreases compression, or both. In particular, the PCTP zinc salt (Example 2) provides comparable COR's with lower compression and/or increased COR's with comparable (or lower) compression, both of which are desirable golf ball properties.

The halogenated organosulfur polymers of the present invention may also be used in golf equipment, in particular, inserts for golf clubs, such as putters, irons, and woods, and in golf shoes and components thereof.

As used herein, the term "about," used in connection with one or more numbers or numerical ranges, should be understood to refer to all such numbers, including all numbers in a range.

The invention described and claimed herein is not to be limited in scope by the specific embodiments herein disclosed, since these embodiments are intended as illustrations of several aspects of the invention. Any equivalent embodiments are intended to be within the scope of this invention. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

What is claimed is:

1. A golf ball comprising:

a core comprising a center having an outer diameter from about 0.375 inches to about 1.4 inches and deflection of greater than about 4.5 mm under a load of 100 kg and an outer core layer having an outer diameter of from about 1.4 inches to about 1.62 inches, wherein the center and core layer are formed from a polybutadiene rubber composition comprising a halogenated organosulfur compound or a metal salt thereof, and

a cover comprising an inner cover layer having an outer diameter of greater than about 1.58 inches and a material hardness of less than about 72 Shore D and an outer cover layer having a hardness of greater than about 50 Shore D and a material hardness of less than about 50 Shore D;

wherein the outer cover layer comprises a polyurea composition.

2. The golf ball of claim 1, wherein the inner cover layer has a material hardness of between about 60 and about 70 Shore D and an outer diameter of about 1.59 in to about 1.66 inches.

3. The golf ball of claim 1, wherein the center has an outer diameter between about 0.5 inches and about 1.25 inches.

4. The golf ball of claim 1, wherein the outer core layer outer diameter is from about 1.52 inches to about 1.58 inches.

5. The golf ball of claim 1, wherein the center has a first hardness, the outer core layer has a second hardness greater

than the first, the inner cover layer has a third hardness greater than the second, and the outer cover layer has a fourth hardness less than the third hardness.

6. The golf ball of claim 1, wherein at least one of the inner or outer cover layers have a thickness of less than about 0.05 inches.

7. The golf ball of claim 1, wherein the halogenated organosulfur compound is selected from the group consisting of pentafluorothiophenol; 2-fluorothiophenol; 3-fluorothiophenol; 4-fluorothiophenol; 2,3-fluorothiophenol; 2,4-fluorothiophenol; 3,4-fluorothiophenol; 3,5-fluorothiophenol; 2,3,4-fluorothiophenol; 3,4,5-fluorothiophenol; 2,3,4,5-tetrafluorothiophenol; 2,3,5,6-tetrafluorothiophenol; 4-chlorotetrafluorothiophenol; pentachlorothiophenol; 2-chlorothiophenol; 3-chlorothiophenol; 4-chlorothiophenol; 2,3-chlorothiophenol; 2,4-chlorothiophenol; 3,4-chlorothiophenol; 3,5-chlorothiophenol; 2,3,4-chlorothiophenol; 3,4,5-chlorothiophenol; 2,3,4,5-tetrachlorothiophenol; 2,3,5,6-tetrachlorothiophenol; pentabromothiophenol; 2-bromothiophenol; 3-bromothiophenol; 4-bromothiophenol; 2,3-bromothiophenol; 2,4-bromothiophenol; 3,4-bromothiophenol; 3,5-bromothiophenol; 2,3,4-bromothiophenol; 3,4,5-bromothiophenol; 2,3,4,5-tetrabromothiophenol; 2,3,5,6-tetrabromothiophenol; pentaiodothiophenol; 2-iodothiophenol; 3-iodothiophenol; 4-iodothiophenol; 2,3-iodothiophenol; 2,4-iodothiophenol; 3,4-iodothiophenol; 3,5-iodothiophenol; 2,3,4-iodothiophenol; 3,4,5-iodothiophenol; 2,3,4,5-tetraiodothiophenol; 2,3,5,6-tetraiodothiophenol; metal salts thereof, and mixtures thereof.

8. The golf ball of claim 7, wherein the halogenated organosulfur compound is pentachlorothiophenol or the metal salt thereof, wherein the metal salt is selected from the group consisting of zinc, calcium, magnesium, sodium, and lithium.

9. A golf ball comprising:

a core comprising a solid center having an outer diameter from about 0.375 inches to about 1.4 inches and deflection of greater than about 4.5 mm under a load of 100 kg and an outer core layer having an outer diameter of from about 1.4 inches to about 1.62 inches, and

a cover comprising an inner cover layer having an outer diameter of greater than about 1.58 inches and a material hardness of less than about 72 Shore D and an outer cover layer comprising polyurea and having a hardness of greater than about 50 Shore D and a material hardness of less than about 50 Shore D

wherein the center and core layer comprise polybutadiene rubber composition comprising a halogenated organosulfur compound or a metal salt thereof.

10. The golf ball of claim 9, wherein the inner cover layer has a material hardness of between about 60 and about 70 Shore D and an outer diameter of about 1.59 inches to about 1.66 inches.

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11. The golf ball of claim 9, wherein the center has an outer diameter between about 0.5 inches and about 1.25 inches.

12. The golf ball of claim 9, wherein the outer core layer outer diameter is from about 1.52 inches to about 1.58 inches.

13. The golf ball of claim 9, wherein the center has a first hardness, the outer core layer has a second hardness greater than the first, the inner cover layer has a third hardness greater than the second, and the outer cover layer has a fourth hardness less than the third hardness.

14. The golf ball of claim 9, wherein at least one of the inner or outer cover layers have a thickness of less than about 0.05 inches.

15. The golf ball of claim 9, wherein the inner cover layer comprises ionomers, vinyl resins, polyolefins, polyurethanes, polyureas, polyamides, acrylic resins, thermoplastics, polyphenylene oxide resins, thermoplastic polyesters, thermoplastic rubbers, fully-neutralized polymers, partially-neutralized polymers, or mixtures thereof.

16. The golf ball of claim 9, wherein the polyurea composition is light stable.

17. The golf ball of claim 9, wherein the halogenated organosulfur compound is selected from the group consisting of pentafluorothiophenol; 2-fluorothiophenol; 3-fluorothiophenol; 4-fluorothiophenol; 2,3-fluorothiophenol; 2,4-fluorothiophenol; 3,4-fluorothiophenol; 3,5-fluorothiophenol; 2,3,4-fluorothiophenol; 3,4,5-fluorothiophenol; 2,3,4,5-tetrafluorothiophenol; 2,3,5,6-tetrafluorothiophenol; 4-chlorotetrafluorothiophenol; pentachlorothiophenol; 2-chlorothiophenol; 3-chlorothiophenol; 4-chlorothiophenol; 2,3-chlorothiophenol; 2,4-chlorothiophenol; 3,4-chlorothiophenol; 3,5-chlorothiophenol; 2,3,4-chlorothiophenol; 3,4,5-chlorothiophenol; 2,3,4,5-tetrachlorothiophenol; 2,3,5,6-tetrachlorothiophenol; pentabromothiophenol; 2-bromothiophenol; 3-bromothiophenol; 4-bromothiophenol; 2,3-bromothiophenol; 2,4-bromothiophenol; 3,4-bromothiophenol; 3,5-bromothiophenol; 2,3,4-bromothiophenol; 3,4,5-bromothiophenol; 2,3,4,5-tetrabromothiophenol; 2,3,5,6-tetrabromothiophenol; pentaiodothiophenol; 2-iodothiophenol; 3-iodothiophenol; 4-iodothiophenol; 2,3-iodothiophenol; 2,4-iodothiophenol; 3,4-iodothiophenol; 3,5-iodothiophenol; 2,3,4-iodothiophenol; 3,4,5-iodothiophenol; 2,3,4,5-tetraiodothiophenol; 2,3,5,6-tetraiodothiophenol; metal salts thereof, and mixtures thereof.

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18. The golf ball of claim 17, wherein the halogenated organosulfur compound is pentachlorothiophenol or the metal salt thereof, wherein the metal salt is selected from the group consisting of zinc, calcium, magnesium, sodium, and lithium.

19. A golf ball comprising:

a core comprising a solid center having an outer diameter from about 0.375 inches to about 1.4 inches and deflection of greater than about 4.5 mm under a load of 100 kg and an outer core layer having an outer diameter of from about 1.4 inches to about 1.62 inches, wherein the center and core layer comprise a polybutadiene rubber composition comprising pentachlorothiophenol or the metal salt thereof, and wherein the metal salt is selected from the group consisting of zinc, calcium, magnesium, sodium, and lithium, and

a cover comprising an inner cover layer having an outer diameter of greater than about 1.58 inches and a material hardness of less than about 72 Shore D and an outer cover layer comprising polyurea and having a hardness of greater than about 50 Shore D and a material hardness of less than about 50 Shore D, at least one of the inner or outer cover layers having a thickness of less than about 0.05 inches.

20. A golf ball comprising:

a core comprising a solid center having a first hardness, an outer diameter from about 0.375 inches to about 1.4 inches, and a deflection of greater than about 4.5 mm under a load of 100 kg, and an outer core layer having a second hardness and an outer diameter of from about 1.4 inches to about 1.62 inches, wherein the center and core layer comprise a polybutadiene rubber composition comprising pentachlorothiophenol or the metal salt thereof, and wherein the metal salt is selected from the group consisting of zinc, calcium, magnesium, sodium, and lithium; and

a cover comprising an inner cover layer having a third hardness, an outer diameter of greater than about 1.58 inches, and a material hardness of less than about 72 Shore D, and an outer cover layer comprising polyurea and having a fourth hardness of less than about 50 Shore D, at least one of the inner or outer cover layers having a thickness of less than about 0.05 inches;

wherein the second hardness is greater than the first, the third hardness is greater than the second hardness, and the fourth hardness is less than the third hardness.

\* \* \* \* \*

# Exhibit 14

United States Patent

[19]

Rajagopalan et al.

[45]

Patent Number:

6,100,340

Date of Patent:

\*Aug. 8, 2000

[54]	GOLF BALL COMPOSITIONS CONTAINING HIGH CRYSTALLINE ACID COPOLYMERS AND THEIR IONOMER DERIVATIVES	4,351,931	9/1982	Armitage	526/227
		4,526,375	7/1985	Nakade	273/235 R
		4,801,649	1/1989	Staz	525/221
		4,884,814	12/1989	Sullivan	273/235 R
		4,911,451	3/1990	Sullivan et al.	273/235 R
		5,000,459	3/1991	Isaac	273/235 R
		5,028,674	7/1991	Hatch et al.	526/216
		5,120,791	6/1992	Sullivan	525/196
		5,197,740	3/1993	Pocklington et al.	273/235 R
		5,324,783	6/1994	Sullivan	525/196
		5,415,937	5/1995	Cadorniga et al.	428/407
		5,553,852	9/1996	Higuchi et al.	473/373
		5,567,772	10/1996	Hagman	525/221
		5,580,927	12/1996	Chou et al.	525/201
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[73]	Assignees: Acushnet Company, Fairhaven, Mass.; E.I. Dupont DeNemours & Company, Wilmington, Del.				
[*]	Notice: This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(a)(2).				
[21]	Appl. No.: 08/783,952				
[22]	Filed: Jan. 16, 1997				
[51]	Int. Cl. <sup>7</sup> A63B 37/12; A63B 37/06				
[52]	U.S. Cl. 525/221; 525/330.2; 526/318.6; 473/371; 473/372; 473/378; 473/385				
[58]	Field of Search 525/330.2, 221; 473/372, 385, 371, 378; 526/318.6				
[56]	References Cited				
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	3,264,272 8/1966 Rees 260/78.5				
	3,819,768 6/1974 Molitor 260/897 B				
	4,248,990 2/1981 Pieski et al 526/317				
	FOREIGN PATENT DOCUMENTS				
	9524448 9/1995 WIPO .				
	Primary Examiner—David Buttner				
	Attorney, Agent, or Firm—Pennie & Edmonds LLP				
[57]	ABSTRACT				
	This invention is directed towards golf balls comprising at least a cover and a core, and optionally one or more intermediate layers, wherein the cover and/or the intermediate layer(s) are formed from a high crystalline copolymer or its ionomer derivatives and blends thereof, wherein the high crystalline copolymer is formed from an ethylene/carboxylic acid copolymer comprising about 5 to about 35 percent by weight acrylic or methacrylic acid, wherein the copolymer is polymerized at a temperature of about 130° C. to 200° C. at pressures of at least 20,000 psi to about 50,000 psi, wherein up to about 70 percent of the acid groups are neutralized with a metal ion.				
	27 Claims, No Drawings				

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**GOLF BALL COMPOSITIONS CONTAINING  
HIGH CRYSTALLINE ACID COPOLYMERS  
AND THEIR IONOMER DERIVATIVES**

**FIELD OF THE INVENTION**

This invention relates to golf balls comprising at least a cover and a core wherein the cover is formed from a high crystalline acid copolymer or its ionomer derivative or a blend of a high crystalline acid copolymer or its ionomer derivatives and at least one additional material, preferably a second acid copolymer or its ionomer derivatives. This invention is additionally directed towards a golf ball which further comprises, in addition to a cover and a core, one or more intermediate layers interposed between the cover and the core, wherein at least one such intermediate layer is formed from a high crystalline acid copolymer or its ionomer derivatives or a blend of a high crystalline acid copolymer or its ionomer derivatives and at least one additional material, preferably a second acid copolymer or its ionomer derivatives.

**BACKGROUND OF THE INVENTION**

Generally, there are four types of golf balls on the market today, i.e., one-piece balls, two-piece balls, wound balls, and recently, multilayer balls. One-piece balls are solid balls of a homogeneous construction which are typically used as practice or range balls. Two piece balls are formed by molding a cover around a solid core. Wound balls are formed by winding a thin elastic thread around a liquid filled or solid core to form a wound center upon which a cover is molded. Multilayer balls can have a variety of constructions, such as having multiple core layers, an intermediate or mantle layer(s) or multiple cover layers and combinations thereof.

The composition of a golf ball's cover has been found to affect on the overall performance of the golf ball, including such parameters as its distance, spin rate, "click" and feel etc. Historically, balata, i.e., a trans polyisoprene rubber, was employed as a cover material. Balata provides a soft cover with excellent spin and feel characteristics which enable a skilled golfer to control the flight of the ball by imparting desirable spin on the ball. However, although balata covers exhibit enhanced playability characteristics, they lack the durability properties required for repetitive play. Likewise, balata is expensive and requires time-consuming and labor-intensive manufacturing procedures.

In the middle 1960's, E.I. DuPont de Nemours Company, Inc. developed a new species of resins known as ionomers or ionomer resins. These resins are sold, inter alia, under the trademark SURLYN®, and have essentially replaced balata as a golf ball cover stock material. Ionomeric resins are typically ionic copolymers of an olefin, e.g., ethylene, and an unsaturated carboxylic acid, such as acrylic acid, methacrylic acid or maleic anhydride or itaconic acid or anhydride which has been partially neutralized, e.g., with a metal ion. In some cases an additional softening comonomer such as a long chain alkyl acrylate is also included to form a terpolymer. Such ionomers are usually distinguished by the type of metal ions, the amount of acid and the degree of neutralization.

Ionomer resins are effectively crosslinked at "use" temperatures, but exhibit thermoplastic processability at melt temperatures. Ionomer resins typically exhibit a relatively high tensile strength, good clarity, high abrasion resistance, high stiffness and high resiliency.

The early ionomer resins produced extremely durable covers and imparted improved flight distance to the balls.

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However, these materials were very hard and therefore lacked the desirable click and feel of balata balls. Moreover, because standard prior art ionomer covers are very hard, it is not possible to impart the desirable spin characteristics to the ball required by the more skilled golfer.

It was subsequently discovered that the physical properties of ionomer resins could be modified according to the amount and type of metal ion, the molecular weight, the composition of the base resin (i.e. the nature and relative content of the olefin, the unsaturated carboxylic acid groups, etc.), the amount of acid, the degree of neutralization and the addition of ingredients such as modifiers, softening agents, etc.

Additionally, in order to overcome some of the negative properties of hard ionomer covers, it became well known that ionomer resins can be blended in order to form ionomer cover compositions that provide improved play characteristics. A number of patents have been granted which are directed towards such ionomer blends.

For example, U.S. Pat. No. 3,819,768 to Molitor discloses golf ball covers comprising blends of zinc and sodium ionomers, which overcome cold cracking problems.

U.S. Pat. No. 4,526,375 to Nakade discloses covers comprising a single ionomer in which a portion of the carboxylic acid groups has been neutralized with sodium, while another portion has been neutralized with magnesium or zinc to overcome a cold cracking problem in covers comprising a single ionomer and a fatigue fracture problem in covers comprising sodium/zinc ionomer blends.

U.S. Pat. No. 4,884,814 to Sullivan discloses golf ball covers comprising blends of a high flexural modulus (hard) ionomer and a low flexural modulus (soft) ionomer. The hard ionomers are copolymers of an olefin and an unsaturated monocarboxylic acid, neutralized with sodium or zinc, and have a flexural modulus of about 30,000 to 55,000 p.s.i. and a Shore D hardness of about 60 to 66. The soft ionomers are terpolymers of an olefin, an unsaturated monocarboxylic acid, and an acrylate ester. These terpolymers are neutralized with zinc or sodium, and have a flexural modulus of about 3,000 to 7,000 p.s.i. and a Shore D hardness of about 25 to 40.

U.S. Pat. No. 4,911,451 to Sullivan et al. discloses a golf ball cover including about 10 to 90 percent by weight of an ethylene-acrylic acid copolymer, containing about 11 percent by weight acrylic acid with about 40 percent of the carboxylic acid groups neutralized with sodium, and about 90 to 10 percent by weight of at least one ethylene-acrylic acid copolymer, containing about 11 to 16 percent acrylic acid with about 10 to 40 percent of the carboxylic acid groups neutralized with zinc.

U.S. Pat. No. 5,000,459 to Isaac discloses golf ball covers made from a lithium ionomer resin, wherein up to 50 percent of the lithium ionomer resin is replaced with at least one sodium ionomer resin. The resulting golf balls are found to be comparable in durability and initial velocity to golf balls having a cover formed with lithium ionomer only.

U.S. Pat. No. 5,120,791 to Sullivan discloses golf ball cover compositions containing blends of at least one hard ionomeric resin, preferably an acrylic acid ionomer, and at least one acrylic acid based soft ionomer. Hard ionomers neutralized with sodium, zinc, magnesium, or lithium, having a flexural modulus of 28 to 55 p.s.i. and a Shore D hardness of 60 to 66 are disclosed. The disclosed soft ionomers are sodium or zinc neutralized terpolymers of an olefin, acrylic acid, and an unsaturated acrylate ester monomer, and have a flexural modulus of about 2,000 to 10,000 p.s.i. and a Shore D hardness of about 20 to 50.

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U.S. Pat. No. 5,324,783 to Sullivan discloses golf ball covers which include a blend of about 10 to 30 weight percent of soft ionomer resins and about 90 to 70 weight percent of hard ionomer resins. The soft ionomers are terpolymers of an olefin, acrylic or methacrylic acid, and an unsaturated acrylate ester.

U.S. Pat. No. 5,415,937 to Cadorniga et al. discloses a golf ball cover material of a blend of 80–50% of a high stiffness ionomer and 20 to 50% of a very low modulus ionomer (“VLMI”) to improve the feel and playability of the ball when compared to a standard ionomer cover, while retaining the distance and resilience of the prior art balls.

However, heretofore, there have not been any disclosures in the prior art directed towards forming golf ball covers and/or intermediate layers from a high crystalline ionomer or a blend of a high crystalline ionomer and at least one additional ionomer.

It has now been found that golf balls with covers and/or an intermediate layer(s) formed from a high crystalline acid copolymer or its ionomer derivatives or a blend of a high crystalline acid copolymer or its ionomer derivatives and at least one additional material, preferably a second acid copolymer or its ionomer derivatives exhibit desirable properties such as increased initial velocity (as compared to “conventional”, i.e., non-high crystalline ionomer blends) without any adverse impact on the remaining golf ball properties such as hardness, compression, durability and spin rate. The present application is therefore directed towards golf balls constructed with covers and/or intermediate layers formed from such compositions, as well as methods for making such golf balls.

SUMMARY OF THE INVENTION

The present invention relates to a golf ball comprising at least a cover and a core, wherein the cover is formed from: a) a high crystalline acid copolymer or its ionomer derivatives formed from a ethylene/carboxylic acid copolymer comprising about 5 to about 35 percent by weight acrylic or methacrylic acid, wherein the copolymer is polymerized at a temperature of about 130° C. to about 200° C. and a pressure of about 20,000 psi to about 50,000 psi and wherein up to about 70 percent of the acid groups are neutralized with a metal ion; or b) a blend of such a high crystalline acid copolymer or its ionomer derivatives and at least a second material, preferably a second acid copolymer or its ionomer derivatives wherein said second acid copolymer is a conventional acid copolymer or a very low modulus acid copolymer or a high acid copolymer or a second high crystalline acid copolymer.

The present invention is still further directed towards a golf ball comprising at least a cover and a core and one or more intermediate layers interposed between the cover and the core, wherein the cover, the intermediate layer(s) or both are formed from: a) a high crystalline acid copolymer or its ionomer derivatives formed from a ethylene/carboxylic acid copolymer comprising about 5 to about 35 percent by weight acrylic or methacrylic acid, wherein the copolymer is polymerized at a temperature of about 130° C. to about 200° C. and a pressure of about 20,000 psi to about 50,000 psi and wherein up to about 70 percent of the acid groups are neutralized with a metal ion; or b) a blend of such a high crystalline acid copolymer or its ionomer derivatives and at least a second material, preferably a second acid copolymer or its ionomer derivatives wherein said second acid copolymer is a conventional acid copolymer, a very low modulus acid copolymer, a high acid copolymer or a second high crystalline acid copolymer or a high flow acid copolymer.

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DETAILED DESCRIPTION OF THE INVENTION

Covers and/or intermediate layers of the golf balls of the present invention are formed from a high crystalline acid copolymer and its ionomer derivatives or a blend of a high crystalline acid copolymer and its ionomer derivatives and at least one additional material, preferably an acid copolymer and its ionomer derivatives. As used herein, the term “high crystalline acid copolymer” is defined as a “product-by-process” in which an acid copolymer or its ionomer derivatives formed from a ethylene/carboxylic acid copolymer comprising about 5 to about 35 percent by weight acrylic or methacrylic acid, wherein the copolymer is polymerized at a temperature of about 130° C. to 200° C., at pressures above about 20,000 psi up to about 50,000 psi, preferably at about 25,000 psi or above, wherein up to about 70 percent of the acid groups are neutralized with a metal ion. The copolymer can have a melt index (“MI”) of from about 20 to about 300 g/10 min., preferably about 20 to about 200 g/10 minutes and upon neutralization of the copolymer, the resulting acid copolymer and its ionomer derivatives should have an MI of from 0.1 to 30.0 g/10 min.

Suitable high crystalline acid copolymer and its ionomer derivatives compositions and methods for making them are disclosed in U.S. Pat. No. 5,580,927, the disclosure of which is hereby incorporated by reference in its entirety.

The high crystalline acid copolymer or its ionomer derivatives employed in the present invention are preferably formed from a copolymer containing about 5–35 percent, more preferably 9–18, most preferably about 10–13 percent, by weight of acrylic acid, wherein up to about 75 percent, most preferably 60 percent, of the acid groups are neutralized with a metal ion, preferably a sodium, lithium, magnesium or zinc ion.

Generally speaking, high crystalline acid copolymer and its ionomer derivatives are formed by polymerization of their base copolymers at lower temperatures, but at equivalent pressures to those used for forming a conventional acid copolymer and its ionomer derivatives. Conventional acid copolymers are typically polymerized at a polymerization temperature of from at least 200° C. to about 270° C., preferably about 220° C., and at pressures of from about 23,000 to about 30,000 psi. In comparison, the high crystalline acid copolymer and its ionomer derivatives employed in the present invention are produced from acid copolymers that are polymerized at a polymerization temperature of less than 200° C., and preferably from about 130° C. to about 200° C., and at pressures from about 20,000 to about 50,000 psi.

As a result of polymerizing the copolymers at lower temperatures, there is a reduction in the presence of undesirable chemical defects in the polymer chains of the resultant acid copolymer and its ionomer derivatives, including a reduction in short chains and branching of the polymer as a result of the better ordering of the polymer chains. Further, a reduction in such defects results in a polymer which has a higher degree of crystallinity than conventional acid copolymers, thereby resulting in a polymer with an increased melting and freezing point.

In accordance with the present invention, it has been found that high crystalline acid copolymers or their ionomer derivatives can be used either alone or in a blend with other materials, preferably, but not limited to acid copolymers or their ionomer derivatives (e.g., conventional acid copolymer, high acid copolymer, very low modulus acid copolymer, high flow acid copolymer and/or other high

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crystalline acid copolymers) for forming golf ball cover compositions and/or intermediate layer(s) to provide a ball with improved in-play characteristics, including an increased initial velocity. Additionally, it is believed that high crystalline acid copolymers or their ionomer derivatives can also be blended with other non-ionic materials.

As discussed above, copolymers of ethylene and an unsaturated carboxylic acid such as (meth)acrylic acid, optionally with another comonomer, and their ionomer derivatives are well known. These conventional copolymers typically contain at least 50 weight percent and up to about 95 weight percent ethylene. Typical commercial ionomer derivatives, such as those sold under the trade name SUR-LYNO by E.I. du Pont de Nemours and Company, derive from acid copolymers with about 5 to 35 weight percent (meth)acrylic acid comonomer. As normally prepared, both the acid copolymers and their ionomer derivatives have differential scanning calorimetry (DSC) melting points which are in the region of about 81 to about 96° C., and freezing points in the region of about 40 to about 60° C., depending on the comonomers and amounts thereof present.

In particular, the conventional acid copolymers and their ionomer derivatives (i.e., non-high crystalline) useful in the blends of the present invention are obtained by providing a cross metallic bond to polymers of monoolefin with at least one member selected from the group consisting of unsaturated mono- or di-carboxylic acids having 3 to 12 carbon atoms and esters thereof (the polymer contains 1 to 50 percent by weight of the unsaturated mono- or di-carboxylic acid and/or ester thereof). More particularly, such acid-containing ethylene copolymer ionomer component includes E/X/Y copolymers where E is ethylene, X is a softening comonomer such as acrylate or methacrylate present in 0–50 (preferably 0–25, most preferably 0–20), weight percent of the polymer, and Y is acrylic or methacrylic acid present in 5–35 (preferably 10–35, more preferably at least about 16–35, most preferably at least about 16–20) weight percent of the polymer, wherein the acid moiety is neutralized 1–90 percent (preferably at least 40 percent, most preferably at least about 60 percent) to form an acid copolymer and its ionomer derivatives by a cation such as lithium\*, sodium\*, potassium, magnesium\*, calcium, barium, lead, tin, zinc\* or aluminum (\*=preferred), or a combination of such cations. Specific acid-containing ethylene copolymers include ethylene/acrylic acid, ethylene/methacrylic acid, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/n-butyl acrylate, ethylene/methacrylic acid/iso-butyl acrylate, ethylene/acrylic acid/iso-butyl acrylate, ethylene/methacrylic acid/n-butyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacrylate. Preferred acid-containing ethylene copolymers include ethylene/methacrylic acid, ethylene/acrylic acid, ethylene/methacrylic acid/n-butyl acrylate, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/methyl acrylate and ethylene/acrylic acid/methyl acrylate copolymers. The most preferred acid-containing ethylene copolymers are ethylene/methacrylic acid, ethylene/acrylic acid, ethylene/(meth)acrylic acid/n-butyl acrylate, ethylene/(meth)acrylic acid/ethyl acrylate, and ethylene/(meth)acrylic acid/methyl acrylate copolymers.

Methods of preparing conventional acid copolymers and their ionomer derivatives are well known. Acid copolymers and their ionomer derivatives can be prepared by the method disclosed in U.S. Pat. No. 4,351,931 (Armitage). This patent

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describes polymers with up to 90 weight percent ethylene, the balance being a carboxylic acid. U.S. Pat. No. 5,028,674 (Hatch et al.) discloses improved methods of polymerizing such copolymers when polar monomers such as acrylic and methacrylic acid are incorporated particularly at a level of higher than 10 weight percent. The preparation of ionomers from acid copolymers is also disclosed in U.S. Pat. No. 3,264,272 (Rees). This is a broad disclosure describing preparation when the starting MI as high as 1000 g/10 minutes, and the MI at the completion of the reaction may be as low as about 0.1 g/10 minutes.

Further, U.S. Pat. No. 4,248,990 (Pieski) describes preparation and properties of acid copolymers at low polymerization temperatures and normal temperatures, as well as low pressures and normal temperatures. Preparation is exemplified by Pieski when the polymerization temperature is as low as 160° C., but also up to 250° C. at normal pressures. The above four patents are hereby incorporated by reference in their entirety.

As also discussed above, blending several ionomers and/or acid copolymers is also well known, and for typical acid copolymers/ionomers which have acid levels of about 9 weight percent and above, incompatibility is not a problem. It is believed that ions are sufficiently labile so that even when ionomers are neutralized with different ions, and/or have different acid levels, different acid monomers, and even third monomers, as well as different levels of neutralization, all ions present will become essentially randomly distributed and associated with all acid groups present in the blend. The ions will be fairly randomly distributed throughout the mix of (chemically) differing underlying polymer chains.

In a first embodiment of the present invention, a golf ball cover and/or intermediate layer(s) is formed from a single high crystalline acid copolymer or its ionomer derivatives. The high crystalline acid copolymer is prepared from a ethylene/carboxylic acid copolymer comprising about 5 to about 35 percent by weight acrylic or methacrylic acid, wherein the copolymer is polymerized at a temperature of about 130° C. to 200° C., at pressures above 20,000 psi up to 50,000 psi, preferably at 25,000 psi or above, wherein up to about 70 percent of the acid groups are neutralized with a metal ion. When substantially the entire cover is comprised of a single high crystalline acid copolymer and its ionomer derivatives composition, the composition is preferably prepared from a ethylene/carboxylic acid copolymer polymerized at a temperature of about 175° C. to about 200° C. and at from 23,000 to 30,000 psi. The copolymer can have a MI of from 20 to 300 g/10 min., preferably 20 to 200 g/10 min. and upon neutralization of the copolymer, the resulting acid copolymer and its ionomer derivatives should have a MI of from 0.1 to 30.0 g/10 min.

Optionally, the high crystalline acid copolymer and its ionomer derivatives may also include up to about 40 percent by weight, preferably about 10 to about 40 percent by weight, and most preferably about 15–30 percent by weight long chain alkyl acrylate or methacrylate whose alkyl group has from 1 to 8 carbon atoms, e.g., iso-butyl or n-butyl acrylate.

In a second embodiment of the present invention, a cover and/or intermediate layer(s) is formed from at least a first component comprising an acid copolymer or its ionomer derivatives and a second component comprising an acid copolymer or its ionomer derivatives, wherein the first component comprises a high crystalline acid copolymer. The second component may comprise any type of acid copolymer or its ionomer derivatives, including the high crystalline

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acid copolymers described above. Among the preferred second components are a second high crystalline acid copolymer, a high acid copolymer or a very low modulus acid copolymer.

As used herein, the term "high acid copolymer" is defined as an acid copolymer or its ionomer derivatives which contains at least about 16 percent acid, preferably from about 16 percent to about 35 percent acid, more preferably from about 19 percent to about 22 percent acid and most preferably about 19 percent acid, wherein 10 to 90 percent of the acid is partially neutralized with sodium, manganese, lithium, potassium, zinc, magnesium, calcium or nickel ions. High acid copolymer ionomers are commercially available from DuPont under the tradename SURLYN. Examples of suitable high acid ionomers include SURLYN 8140 (Na), SURLYN 8546 (Li), SURLYN 8240 (Na) and SURLYN 8220 (Na).

As used herein, "very low modulus acid copolymer" (VLM) are defined as terpolymers comprising of 65 to 70 percent by weight of ethylene, about 20 to 25 percent by weight of n- or iso-butyl-acrylate, and about 10 percent by weight of methacrylic acid, where 10 to 90 percent of the acid groups are neutralized by sodium, zinc, or lithium ions. The VLM preferably have a melt index of 0.5 to 10 g/10 min, a Shore D hardness of 20 to 50, and a flexural modulus of 2,000 to 8,000. Suitable VLMI are commercially available from DuPont under the tradename SURLYN. Suitable very low modulus acid ionomer derivatives include SURLYN 8320 (Na), SURLYN 9320 (Zn) and SURLYN 8120 (Na).

In this second embodiment of the invention, the composition is formed from a blend which comprises at least 1, preferably about 5 to about 95, more preferably 10-80, and most preferably about 30-50, percent by weight of the first component and about 99, preferably about 95 to about 5, more preferably 90-20 and most preferably about 70 to about 50 percent by weight of the second component.

In a third embodiment of the invention, the cover and/or intermediate layer(s) composition is formed from a blend of a first component comprising an acid copolymer or its ionomer derivatives, a second component comprising acid copolymer or its ionomer derivatives and a third component wherein acid copolymer or its ionomer derivatives, wherein the first component is a high crystalline acid copolymer and the second and third acid components are selected from among high crystalline acid copolymer, high acid copolymer, very low modulus acid copolymer, high flow acid copolymers and conventional acid copolymers, with the caveat that the second and third acid components are different materials from each other.

In this embodiment of the invention, the cover composition is formed from a blend which comprises at least about 1, preferably about 10 to about 90 and most preferably about 25 to about 75 percent by weight of the first component; about 49.5, preferably about 45 to about 5.0, and most preferably about 37.5 to about 12.5 percent by weight of the second component; and about 49.5, preferably about 45 to about 5.0 and most preferably about 37.5 to about 12.5 percent by weight of the third component.

The acid copolymer/ionomer derivative blends of the present invention preferably have a MI of from 0.1 to 7.0 g/10 min. Thus, if one blend component has a high MI of, for example, 30 g/10 min. there should be a sufficient amount of a low MI second component to reduce the final MI to no more than about 7.0 g/10 minute.

Because blending averages out the level of neutralization, (as well as MI) it is possible to blend acid copolymer/ionomer derivatives having a relatively low level of neutralization, such as 10 percent, with one having a higher

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level of neutralization provided the overall level of neutralization is above about 25 percent, but less than about 70 percent. While maximum ionomer character (e.g. abrasion and cut resistance) is desirable, there will be a balance between increasing neutralization level to achieve such ionomer character, and keeping it lower to prevent undue reduction in melting and freezing points. Preferably, the overall level of neutralization is below 40 percent.

The blends employed in the present invention can be formed by combining the polymer components by methods familiar to those in the blending art, for example with a two roll mill, a Banbury Mixer, or a single or twin screw extruder, to produce a compatible blend.

The high crystalline acid copolymers or their ionomer derivatives and blends thereof of the present invention can be employed to form the outer cover layer of any type of golf ball construction, i.e., two-piece, wound or multilayer constructions. The cover compositions can be formed about the core construction of such balls using conventional molding techniques (i.e., injection or compression molding) and do not require any special equipment or modification of standard processing techniques.

Further, the high crystalline acid copolymer or their ionomer derivatives and blends thereof of the present invention may also be employed to form any one of the intermediate layers of a multilayer ball. For example, such balls may have a dual cover construction wherein a conventional core is surrounded by a cover which comprises an inner cover layer and an outer layer. Additionally, and/or alternatively, the multilayer ball may also contain an intermediate mantle layer disposed between the core and the cover layer. The mantle layer and/or the core may also comprise a plurality of layers. By the present invention, it is contemplated that, in addition to the cover per se, any interior layer such as an inner cover layer or one or more mantle and/or core layers may be formed from a high crystalline acid copolymer or its ionomer derivatives or blends containing a high crystalline acid copolymer or its ionomer derivatives and at least one additional acid copolymer or its ionomer derivatives. Further, both the outer cover layer as well as any intermediate layer(s) of any multilayer construction may both be formed in the same construction from a high crystalline acid copolymer or blends containing a high crystalline acid copolymer and at least one additional acid copolymer or its ionomer derivatives. The over and the intermediate layer may be formed from the same blend or may be formed from different blends.

The following examples of golf balls formed according to the present invention are given to illustrate the invention. However, it is to be understood that the examples are for illustrative purposes only and in no manner is the present invention limited to the specific disclosures therein.

EXAMPLES

Examples 1

Table 1 below provides several batch formulations for golf ball cover compositions, including several embodiments employed in the present invention. The blends are given in parts per weight for each ingredient. Batch Number 1 is a conventional cover composition used as a control composition. The high crystalline SURLYNs® used in these formulations were experimental high crystalline ionomer provided by DuPont which were made in accordance with the disclosure U.S. Pat. No. 5,580,927. These SURLYNs® were formed from copolymers containing about 12% acrylic acid, wherein about 60% of the acid groups were neutralized with sodium, lithium, magnesium or zinc.

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TABLE 1

Blend Formulations for High Crystalline Cover Compositions															
In- gredi- ents	BLEND #1 (Con- trol)	BLEND #2	BLEND #3	BLEND #4	BLEND #5	BLEND #6	BLEND #7	BLEND #8	BLEND #9	BLEND #10	BLEND #11	BLEND #12	BLEND #13	BLEND #14	BLEND #15
SUR- LYN 7940 (Li)	45	—	—	—	—	—	—	—	—	—	—	—	—	—	100
SUR LYN 8320 (Na)	55	55	55	55	55	55	55	55	55	55	—	—	—	—	—
High Crystal- line SUR- LYN (Na)	—	45	—	—	—	10	10	—	10	—	100	—	—	—	—
High Crystal- line SUR- LYN (Na)	—	—	45	—	—	25	25	35	35	35	—	100	—	—	—
High Crystal- line SUR- LYN (Li)	—	—	—	45	—	—	10	—	—	10	—	—	100	—	—
High Crystal- line SUR- LYN (Mg)	—	—	—	—	45	10	—	10	—	—	—	—	—	100	—
WHITE CONC. (Zn)	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5

Using the cover formulations of Table 1, golf balls of a two-piece construction were produced using conventional manufacturing processes. Specifically, a 1.580 inch core comprising a cis 1,4 polybutadiene rubber crosslinked with a metal salt of an unsaturated fatty acid such as zinc diacrylate was employed. Hemispherical cups formed of the cover compositions of the blend formulations in Table 1 were injection molded and subsequently compression molded about the polybutadiene cores using standard molding techniques.

These balls were finished and then tested for cover hardness, initial velocity and Coefficient of Restitution (COR). The cover hardness was obtained using a Shore D Durometer. The initial velocity results were obtained from a conventional dual pendulum technique disclosed in U.S. Pat. No. 2,058,201 to Young whereby the balls are struck at 39.6 m/s (130 ft/s) and pass through light gates from which the speed of the balls is calculated. The results of this testing are reported below in Tables 2–4 below.

TABLE 2

Properties of Golf Balls Having High Crystalline Ionomer Cover Compositions						
		BLEND #1	BLEND #2	BLEND #3	BLEND #4	BLEND #5
Cover	@50° F.	59	59	57	56	54
Hardness	@70° F.	60	60	61	60	57

TABLE 2-continued

Properties of Golf Balls Having High Crystalline Ionomer Cover Compositions						
		BLEND #1	BLEND #2	BLEND #3	BLEND #4	BLEND #5
(Shore D)	@90° F- 24 HRS.	53	54	57	57	52
Initial	@50° F.	248.97	244.96	248.93	249.30	248.86
Velocity	@70° F.	251.33	251.46	251.74	251.06	251.26
(f/s)	@90° F.	251.86	252.26	252.52	252.19	251.86
	@120° F.	252.82	253.51	253.72	253.55	253.22
Coefficient	@50° F.	0.791	0.791	0.795	0.795	0.791
of Restitu-	@70° F.	0.802	0.802	0.802	0.799	0.799
tion	@90° F.	0.809	0.812	0.812	0.811	0.810
@125 f/s	@120° F.	0.813	0.818	0.819	0.817	0.815

TABLE 3

Properties of Golf Balls Having High Crystalline Ionomer Cover Compositions						
		BLEND #6	BLEND #7	BLEND #8	BLEND #9	BLEND #10
Cover	@50° F.	56	57	56	57	55
Hardness	@70° F.	60	61	59	60	60
(Shore D)	@90° F.- 24 HRS.	55	55	54	56	55

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TABLE 3-continued

Properties of Golf Balls Having High Crystalline Ionomer Cover Compositions						
		BLEND #6	BLEND #7	BLEND #8	BLEND #9	BLEND #10
Initial	@50° F.	249.09	249.12	249.37	249.10	248.71
Velocity (f/s)	@70° F.	251.49	251.31	251.64	251.50	251.61
	@90° F.	252.15	252.01	252.06	252.22	252.29
	@120° F.	253.36	253.06	253.40	253.35	253.44
Coefficient of Restitu- tion	@50° F.	0.793	0.794	0.791	0.791	0.788
	@70° F.	0.800	0.802	0.799	0.799	0.800
	@90° F.	0.812	0.811	0.809	0.810	0.811
	@125 f/s	@120° F.	0.815	0.819	0.813	0.817
						0.817

TABLE 4

Properties of Golf Balls Having High Crystalline Ionomer Cover Compositions						
		BLEND #11	BLEND #12	BLEND #13	BLEND #14	BLEND #15
Cover	@50° F.	72	72	71	69	71
Hardness	@70° F.	68	67	68	63	64
	@90° F.	65	65	65	60	63
	24 HRS.					
Initial	@50° F.	251.24	251.06	250.66	250.51	251.09
Velocity (f/s)	@70° F.	252.83	252.55	252.2.1	251.32	253.07
	@90° F.	253.59	253.53	253.18	252.11	253.72
	@120° F.	254.29	254.01	254.28	252.87	254.36
Coefficient of Restitu- tion	@50° F.	0.801	0.799	0.796	0.795	0.805
	@70° F.	0.812	0.810	0.806	0.800	0.812
	@90° F.	0.821	0.811	0.826	0.826	0.821
	@125 f/s	@120° F.	0.827	0.824	0.820	0.810
						0.824

As illustrated by Tables 2–4 above, golf balls having covers containing high crystalline ionomers and blends thereof exhibit improved initial velocity.

Of particular interest is a comparison of the initial velocities reported for the control blend #1 and high crystalline blend #3. This comparison is of particular interest because both cover blends contain 55 parts of SURLYN 8320 (VLMI) and 45 parts of a lithium ionomer (i.e. Surlyn 7940 for Blend #1 and a high crystalline SURLYN for Blend #3). A comparison of the results for these blends reveals that the golf balls of blend #3 typically had an initial velocity of about 0.41 to about 0.90 ft./sec. greater than those of blend #1 as tested at temperatures of 70–120° F. respectively.

One of ordinary skill in the art would readily recognize that such increases represent appreciable increases in initial velocity that would result in greater overall distance.

Example 2

The thermal behavior of various ionomer blends has been investigated. For example, Table 5 below illustrates the thermal behavior of certain specific high crystalline ionomers as compared to non-high crystalline ionomers having similar blend components.

TABLE 5

Thermal Behavior of Ionomers						
BLEND #	COMP. WT. %	% NEUT; ION	POLY. TEMP. (° C.)	Tm (° C.)	Tc (° C.)	HEAT XRYST.
1	E/MAA; 85/15	40; Na	230– 255	88	50	38

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TABLE 5-continued

Thermal Behavior of Ionomers							
BLEND #	COMP. WT. %	% NEUT; ION	POLY. TEMP. (° C.)	Tm (° C.)	Tc (° C.)	HEAT XRYST.	
2	E/MAA; 85/15	59; Na	230– 255	88	47	30	
3	E/MAA; 85/15	30; Na	170	103	81	76	
4	E/MAA; 85/15	60; Na	170	101	61	36	

Poly Temp. = Polymerization Temperature; Tm = peak melting point; Tc = peak freezing point; Heat Xryst = heat of crystallization in Joules/gram

As illustrated above, the high crystalline ionomers exhibit markedly higher melting points, freezing points and heat of crystallization. This is believed to be due to the reduction in short chains and branching of the polymer as a result of the lower polymerization temperature.

While it is apparent that the illustrative embodiments of the invention herein disclosed fulfills the objective stated above, it will be appreciated that numerous modifications and other embodiments may be devised by those skilled in the art. Therefore, it will be understood that the appended claims are intended to cover all such modifications which come within the spirit and scope of the present invention.

We claim:

1. A golf ball comprising a cover and a core, wherein at least one of the cover and the core comprises at least one first acid copolymer or an ionomer derivative of the first acid copolymer formed from an ethylene/carboxylic acid copolymer consisting of ethylene and from about 9 to about 18 percent by weight acrylic or methacrylic acid, wherein the copolymer has a melt index of from 20 to about 300 g/10 min., and is polymerized at a temperature of about 130° C. to 200° C. and a pressure of about 20,000 psi to about 50,000 psi, wherein up to about 70 percent of the acid groups in the ionomer derivative are neutralized with a metal ion, and wherein the first copolymer or an ionomer derivative of the first copolymer has a melting point and a freezing point substantially higher than an acid copolymer or ionomer derivative thereof formed at a polymerization temperature greater than 200° C.

2. The golf ball of claim 1, wherein at least one of the cover or the core further comprises a non-ionic material.

3. The golf ball of claim 1, wherein the copolymer is polymerized at a temperature of at least about 175° C. to 200° C.

4. The golf ball of claim 1, wherein the copolymer is an ionomer derived from an ethylene/carboxylic acid copolymer.

5. The golf ball of claim 4, wherein the ionomer has a melt index of about 0.1 g/10 min. to about 7.0 g/10 min.

6. The golf ball of claim 1, wherein the cover is formed from a blend comprising a first component and a second component, wherein second component is different from the first component.

7. The golf ball of claim 6, wherein the blend comprises at least 1 percent by weight of the first component.

8. The golf ball of claim 6, wherein the blend comprises at least about 10 to about 80 percent by weight of the first component and at least about 90 to about 20 percent by weight of the second component.

9. The golf ball of claim 6, wherein the second component comprises at least one of a second acid copolymer and an ionomer derivative of the second acid copolymer, formed from an ethylene/carboxylic acid polymer comprising about 5 to about 35 percent by weight acrylic or methacrylic acid,

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wherein up to about 70 percent of the acid groups are neutralized with a metal ion.

10. The golf ball of claim 6, wherein the second component is a terpolymer comprising an olefin, about 5 to about 35 percent by weight acrylic or methacrylic acid and at least about 1.0 percent by weight to about 40.0 percent by weight of an alkyl acrylate or methacrylate having an alkyl group of from 1 to 8 carbon atoms.

11. The golf ball of claim 6, wherein the cover is formed by a blend further comprising a third component, wherein the third component is different from the first component and the second component.

12. The golf ball of claim 11, wherein the second component and the third component each comprise at least one material selected from the group consisting of:

- (a) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from an ethylene/carboxylic acid copolymer comprising about 5 to about 35 percent by weight acrylic or methacrylic acid, wherein the copolymer is polymerized at a temperature of about 130° C. to 200° C. and a pressure of about 20,000 psi to about 50,000 psi, and wherein up to about 70 percent of the acid groups are neutralized with a metal ion, and wherein the first copolymer or an ionomer derivative of the first copolymer has a melting point and a freezing point substantially higher than an acid copolymer or ionomer derivative thereof formed at a polymerization temperature greater than 200° C.;
- (b) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from an ethylene/carboxylic acid copolymer which comprises at least 16 to about 30 percent by weight acrylic or methacrylic acid;
- (c) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from a terpolymer which comprises at least about 1.0 percent by weight to about 40.0 percent by weight of an alkyl acrylate or methacrylate having an alkyl group of from 1 to 8 carbon atoms, wherein up to about 70 percent of the acid groups of the terpolymer are neutralized with a metal ion; and
- (d) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from an ionomer comprising an ethylene/carboxylic acid copolymer which comprises about 5 to about 15 percent by weight acrylic or methacrylic acid.

13. The golf ball of claim 11, wherein the blend comprises at least about 10 to about 90 percent by weight of the first component, about 45 to about 5 percent by weight of the second component, and about 45 to about 5 percent by weight of the third component.

14. A method for making a golf ball comprising:

- (a) forming a golf ball core;
- (b) forming a blend comprising a first component and at least one second component different from the first component, wherein the first component comprises at least one of a first acid copolymer and an ionomer derivative of the first acid copolymer, formed from an ethylene/carboxylic acid copolymer consisting of ethylene and from about 9 to about 18 percent by weight acrylic or methacrylic acid, wherein the copolymer has a melt index of from 20 to about 300 g/10 min., and is polymerized at a temperature of about 130° C. to 200° C. and a pressure of about 20,000 psi to about 50,000 psi, and wherein up to about 70 percent of the acid groups are neutralized with a metal ion, and wherein

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the first copolymer or an ionomer derivative of the first copolymer has a melting point and a freezing point substantially higher than an acid copolymer or ionomer derivative thereof formed at a polymerization temperature greater than 200° C.; and

(c) forming a cover from the blend by molding the blend around the golf ball core.

15. The method of claim 14, wherein the first copolymer is polymerized at a temperature of at least about 175° C. to 200° C.

16. The method of claim 14, wherein the blend comprises at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from the second component.

17. The method of claim 14, wherein the first component is an ionomer derived from an ethylene/carboxylic acid copolymer.

18. The method of claim 16, wherein the second component is selected from the group consisting of:

- (a) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from an ethylene/carboxylic acid copolymer comprising about 5 to about 35 percent by weight acrylic or methacrylic acid, wherein the copolymer is polymerized at a temperature of about 130° C. to 200° C. and a pressure of about 20,000 psi to about 50,000 psi, and wherein up to about 70 percent of the acid groups are neutralized with a metal ion, and wherein the first copolymer or an ionomer derivative of the first copolymer has a melting point and a freezing point substantially higher than an acid copolymer or ionomer derivative thereof formed at a polymerization temperature greater than 200° C.;
- (b) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from an ethylene/carboxylic acid copolymer which comprises at least 16 to about 30 percent by weight acrylic or methacrylic acid;
- (c) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from a terpolymer which comprises at least about 1.0 percent by weight to about 40.0 percent by weight of an alkyl acrylate or methacrylate having an alkyl group of from 1 to 8 carbon atoms, wherein 10 to 70 percent of the acid groups are neutralized with a metal ion; and
- (d) at least one of an acid copolymer or an ionomer derivative of the acid copolymer, formed from an ionomer comprising an ethylene/carboxylic acid copolymer which comprises about 5 to about 15 percent by weight acrylic or methacrylic acid.

19. The method of claim 14, wherein the component blend comprises a third component, wherein the third component is different from both the first component and the second component.

20. The method of claim 19, wherein the third component is selected from the group consisting of:

- (a) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from an ethylene/carboxylic acid copolymer comprising about 5 to about 35 percent by weight acrylic or methacrylic acid, wherein the copolymer is polymerized at a temperature of about 130° C. to 200° C. and a pressure of about 20,000 psi to about 50,000 psi, and wherein up to about 70 percent of the acid groups are neutralized with a metal ion, and wherein the first copolymer or an ionomer derivative of the first copolymer has a melting point and a freezing point substantially higher than an acid copolymer or ionomer derivative thereof formed at a polymerization temperature greater than 200° C.;

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- (b) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from an ethylene/carboxylic acid copolymer which comprises at least 16 to about 30 percent by weight acrylic or methacrylic acid;
- (c) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from a terpolymer which comprises at least about 1.0 percent by weight to about 40.0 percent by weight of an alkyl acrylate or methacrylate having an alkyl group of from 1 to 8 carbon atoms, wherein up to about 70 percent of the acid groups are neutralized with a metal ion; and
- (d) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from an ionomer comprising an ethylene/carboxylic acid copolymer which comprises about 5 to about 15 percent by weight acrylic or methacrylic acid.

21. A method for making a golf ball comprising:

- (a) forming a blend comprising a first component and at least one second component different from the first component, wherein the first component comprises at least one of a first acid copolymer and an ionomer derivative of the first acid copolymer, formed from an ethylene/carboxylic acid copolymer comprising about 9 to about 18 percent by weight acrylic or methacrylic acid, wherein the copolymer has a melt index of from 20 to about 300 g/10 min., and is polymerized at a temperature of about 130° C. to 200° C. and a pressure of about 20,000 psi to about 50,000 psi, and wherein up to about 70 percent of the acid groups are neutralized with a metal ion, and wherein the first copolymer or an ionomer derivative of the first copolymer has a melting point and a freezing point substantially higher than an acid copolymer or ionomer derivative thereof formed at a polymerization temperature greater than 200° C.;
- (b) forming a golf ball core from the blend; and
- (c) molding a cover around the golf ball core to form a golf ball.

22. The method of claim 21, wherein the first component is an ionomer derived from an ethylene/carboxylic acid copolymer.

23. The method of claim 21, wherein the first copolymer is polymerized at a temperature of at least about 175° C. to 200° C.

24. The method of claim 21, wherein the blend comprises at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from the second component.

25. The method of claim 21, wherein the second component is selected from the group consisting of:

- (a) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from an ethylene/carboxylic acid copolymer comprising about 5 to about 35 percent by weight acrylic or methacrylic acid, wherein the copolymer is polymerized at a temperature of about 130° C. to 200° C. and a pressure of about 20,000 psi to about 50,000 psi, and wherein up to about 70 percent of the acid groups are neutralized with

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a metal ion, and wherein the first copolymer or an ionomer derivative of the first copolymer has a melting point and a freezing point substantially higher than an acid copolymer or ionomer derivative thereof formed at a polymerization temperature greater than 200° C.;

- (b) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from an ethylene/carboxylic acid copolymer which comprises at least 16 to about 30 percent by weight acrylic or methacrylic acid;
- (c) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from a terpolymer which comprises at least about 1.0 percent by weight to about 40.0 percent by weight of an alkyl acrylate or methacrylate having an alkyl group of from 1 to 8 carbon atoms, wherein up to about 70 percent of the acid groups are neutralized with a metal ion; and
- (d) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from an ionomer comprising an ethylene/carboxylic acid copolymer which comprises about 5 to about 15 percent by weight acrylic or methacrylic acid.

26. The method of claim 21, wherein the component blend comprises a third component, wherein the third component is different from both the first component and the second component.

27. The method of claim 21, wherein the third component is selected from the group consisting of:

- (a) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from an ethylene/carboxylic acid copolymer comprising about 5 to about 35 percent by weight acrylic or methacrylic acid, wherein the copolymer is polymerized at a temperature of about 130° C. to 200° C. and a pressure of about 20,000 psi to about 50,000 psi, and wherein up to about 70 percent of the acid groups are neutralized with a metal ion;
- (b) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from an ethylene/carboxylic acid copolymer which comprises at least 16 to about 30 percent by weight acrylic or methacrylic acid;
- (c) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from a terpolymer which comprises at least about 1.0 percent by weight to about 40.0 percent by weight of an alkyl acrylate or methacrylate having an alkyl group of from 1 to 8 carbon atoms, wherein up to about 70 percent of the acid groups are neutralized with a metal ion; and
- (d) at least one of an acid copolymer and an ionomer derivative of the acid copolymer, formed from an ionomer comprising an ethylene/carboxylic acid copolymer which comprises about 5 to about 15 percent by weight acrylic or methacrylic acid.

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